

Supporting Information

Construction of Methylenecycloheptane Frameworks through 7-*Exo-dig* Cyclization of Acetylenic Silyl Enol Ethers Catalyzed by Triethynylphosphine–Gold Complex

Hideto Ito, Hirohisa Ohmiya and Masaya Sawamura*
*Department of Chemistry, Faculty of Science, Hokkaido University,
Sapporo 060-0810, Japan*

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General.

NMR spectra were recorded on a Varian Gemini 2000 spectrometer, operating at 300 MHz for ^1H NMR, 75.4 MHz for ^{13}C NMR and 121.4 MHz for ^{31}P NMR. Chemical shift values for ^1H , ^{13}C and ^{31}P NMR are reference to Me_4Si , the residual solvent resonances and external aqueous 85% H_3PO_4 respectively. Mass spectrometry (JEOL JMS-FABmate for EI-MS, JEOL JMS-700TZ for ESI-MS) and elemental analysis were performed at the Instrumental Analysis Division, Equipment Management Center, Creative Research Institution, Hokkaido University. Triethynylphosphine ligand **L1** was prepared according to the reported procedure.¹ AgNTf_2 was prepared from Ag_2O and $\text{HN}(\text{SO}_2\text{CF}_3)_2$.² AgSbF_6 , AgBF_4 and AgOTf were purchased from Aldrich. Phosphine ligands, PPh_3 and $\text{P}(\text{O}i\text{Pr})_3$ were commercially available. Gold complexes $[\text{AuCl}(\text{ligand})]$ were synthesized by the reported method.¹ MS4A was purchased from Junsei Chemical Co. Anhydrous solvents used in the synthesis of materials were purchased from Kanto Chemical Co. and used without further purification. Anhydrous CH_2Cl_2 and DCE were purchased from Kanto Chemical Co. and Aldrich, respectively. Anhydrous CH_2Cl_2 , DCE, MeOH, 1.0 M $t\text{BuOH}$ in CH_2Cl_2 and 1.0 M $t\text{BuOH}$ in DCE used in Au-catalyzed cyclizations were degassed and dried with MS4A before use, and their water amount (almost always under 15 ppm) was measured by Karl Fisher's moisture meter (Kyoto Electronics Manufacturing Co. Ltd., MKC-520). Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, CHCl_3 , 3.5 mL/min, UV and RI detectors). TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Kanto Chemical Co., Silica gel 60 N, spherical, neutral) was used for column chromatography. PTLC purification was performed on commercial glass plates bearing 1-mm layer of Merck Silica gel 60F₂₅₄. All reactions were carried out under argon atmosphere unless otherwise noted.

Preparation of Cationic Gold-Phosphine Complexs¹

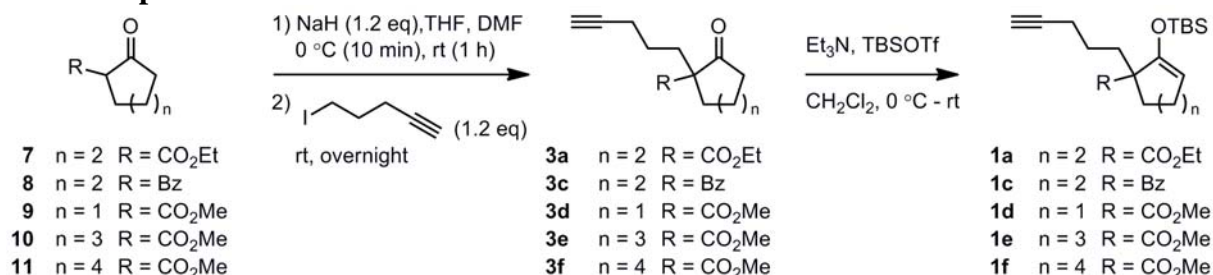
$[\text{AuCl}(\text{ligand})]$ (1 eq) was placed in an open vial tube, and was dissolved in CH_2Cl_2 (ca. 0.1 M). AgX (>1.5 eq) was added, and a mixture was stirred at 25 °C for 10 min. The resulting white suspension was filtered through celite to a screw vial. The resulting colorless solution was first concentrated with a stream of Ar gas, and then was dried *in vacuo* to give $[\text{AuX}(\text{ligand})]$.

General Procedure for Cyclization of Alkynyl Silyl Enol Ethers.

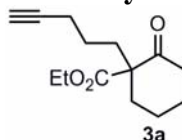
MS4A (ca. 100 mg) was added to a Schlenk tube, and vigorously stirred with heating by heat gun for 5 min in *vacuo*. Then, a flask was cooled to rt and charged with Ar. Au catalyst, CH₂Cl₂ (3.9 mL) and 1.0 M ^tBuOH in CH₂Cl₂ (0.10 mL, 0.10 mmol) were added to a Schlenk tube in this order. The reaction vessel was placed into water bath (for 25 °C or 40 °C) or oil bath (for 80 °C). The alkynyl silyl enol ether (0.10 mmol) was weighed into micro tube and diluted with CH₂Cl₂ (0.25 mL). The mixture was added dropwise to the Schlenk tube by a well dried 250 μ L syringe over 1 min. The substrate solutions remaining in the micro tube and the syringe were washed with CH₂Cl₂ (3 \times 0.25 mL) and added to the reaction mixture. The mixture was stirred at appropriate temperature. After completion of the reaction (monitored by TLC), the resulting mixture was passed through a pad of silica gel and concentrated to dryness. Purification by flash chromatography on silica gel or PTLC gave the cyclization product.

Preparation of Substrates.

Scheme 1. Preparations of 1a and 1c–1f.

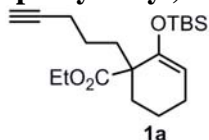


Ethyl 2-Oxo-1-(4-pentyn-1-yl)cyclohexanecarboxylate (3a)



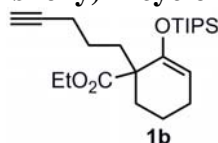
To a suspension of NaH (60 wt. %, 910 mg, 22.8 mmol) in THF (10 mL) and DMF (10 mL) was added dropwise ethyl 2-oxocyclohexanecarboxylate (**7**) (3.28 mL, 20.0 mmol) at 0 °C. The mixture was stirred at this temperature for 10 min and at room temperature for 1 h. Then, 5-iodo-1-pentyne (4.67 g, 24.1 mmol) was added, and the reaction mixture was stirred for 18 h (monitored by TLC). The resulting suspension was diluted with ether, and quenched with saturated aqueous NH₄Cl. The organic layer was washed with saturated aqueous NH₄Cl (3 \times 20 mL), and separated. The combined aqueous layer was extracted with ether (3 \times 20 mL). The organic layers were combined, dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (hexane/EtOAc 99:1 to 92:8) to afford **3a** as a colorless oil (4.68 g, 99%). IR (neat) 636, 1181, 1708, 2941, 3287 cm⁻¹; ¹H NMR (CDCl₃) δ 1.27 (t, *J* = 7.2 Hz, 3H), 1.35–1.80 (m, 7H), 1.89–2.06 (m, 2H), 1.95 (t, *J* = 2.7 Hz, 1H), 2.19 (td, *J* = 6.9, 2.7 Hz, 2H), 2.37–2.56 (m, 3H), 4.24 (q, *J* = 7.2 Hz, 2H). ¹³C NMR (CDCl₃) δ 13.80, 18.43, 22.20, 23.10, 27.25, 33.54, 35.77, 40.74, 60.29, 60.94, 68.42, 83.60, 171.78, 207.72. HRMS (ESI⁺) Calcd for C₁₄H₂₀O₃Na [M+Na]⁺: *m/z* 259.13047. Found: *m/z* 259.13018.

Ethyl 2-(*tert*-Butyldimethylsiloxy)-1-(4-pentyn-1-yl)-2-cyclohexenecarboxylate (1a)



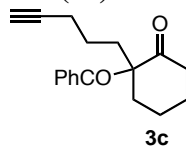
To a solution of **3a** (1.19 g, 5.05 mmol) and Et₃N (1.39 mL, 10.0 mmol) in CH₂Cl₂ (10 mL), TBSOTf (1.76 mL, 7.51 mmol) was added at 0 °C under Ar atmosphere, then the reaction mixture was slowly warmed to room temperature and stirred overnight. The resulting suspension was diluted with ether, and quenched with saturated aqueous NaHCO₃. The organic layer was washed with water (2 × 10 mL) and brine (10 mL), and separated. The combined aqueous layer was extracted with ether (3 × 10 mL). The organic layers were combined, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (hexane/EtOAc 99.5:0.5 to 97:3) provided **1a** as a colorless oil (1.66 g, 94%). IR (neat) 777, 833, 926, 1156, 1662, 1726, 2931, 2951, 3313 cm⁻¹; ¹H NMR (CDCl₃) δ 0.14 (s, 3H), 0.17 (s, 3H), 0.88 (s, 9H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.42–1.72 (m, 5H), 1.88–1.89 (m, 2H), 1.94 (t, *J* = 2.7 Hz, 1H), 1.95–2.08 (m, 3H), 2.19 (td, *J* = 7.2, 2.7 Hz, 2H), 4.03–4.21 (m, 2H), 4.84 (aprox. dd, *J* = 4.5, 3.6 Hz, 1H). ¹³C NMR (CDCl₃) δ -5.46, -4.55, 14.07, 17.85, 18.84, 19.19, 23.57, 23.82, 25.46, 31.81, 34.22, 50.53, 60.34, 68.16, 84.39, 103.93, 149.80, 175.81. Anal. Calcd for C₂₀H₃₄O₃Si: C, 68.52; H, 9.78%. Found: C, 68.21; H, 9.78%.

Ethyl 1-(4-Pentyn-1-yl)-2-(triisopropylsiloxy)-2-cyclohexenecarboxylate (**1b**)

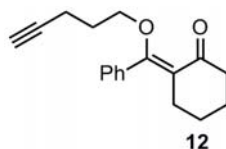


To a solution of **3a** (1.19 g, 5.05 mmol) and 2,6-lutidine (0.399 mL, 3.40 mmol) in CH₂Cl₂ (3.4 mL), TIPSOTf (0.685 mL, 2.55 mmol) was added at 0 °C under Ar atmosphere. Then the reaction mixture was slowly warmed to room temperature and stirred for 18 h. The resulting suspension was diluted with ether, and quenched with saturated aqueous NaHCO₃. The organic layer was washed with water (2 × 5 mL) and brine (5 mL), and separated. The combined aqueous layer was extracted with ether (3 × 5 mL). The organic layers were combined, dried over MgSO₄, filtered and concentrated under reduced pressure. Purification by flash chromatography on silica gel (hexane/EtOAc 99.5:0.5 to 97:3) provided **1b** as a colorless oil (0.645 g, 97%). IR (neat) 624, 881, 925, 1185, 1463, 1662, 1727, 2866, 2943, 3313 cm⁻¹; ¹H NMR (CDCl₃) δ 1.03–1.20 (s, 21H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.52–1.68 (m, 5H), 1.80–2.00 (m, 3H), 1.93 (t, *J* = 2.7 Hz, 1H), 2.19 (td, *J* = 7.2, 2.7 Hz, 2H), 4.00–4.21 (m, 2H), 4.85 (t, *J* = 4.2 Hz, 1H). ¹³C NMR (CDCl₃) δ 12.66, 14.02, 17.97, 18.08, 18.90, 19.15, 23.63, 23.79, 31.74, 34.37, 50.49, 60.35, 68.13, 84.41, 103.16, 150.01, 175.75. HRMS (ESI⁺) Calcd for C₂₃H₄₀O₃SiNa [M+Na]⁺: *m/z* 415.26389. Found: *m/z* 415.26293.

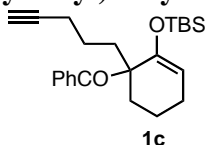
2-Benzoyl-2-(4-pentyn-1-yl)cyclohexanone (**3c**)



The compound **3c** was prepared according to the procedure for the preparation of **3a**, employing 2-benzoylcyclohexanone **8** (2.01 g, 10.0 mmol), NaH (481 mg, 12.0 mmol), 5-iodo-1-pentyne (2.33 g, 12.0 mmol) and hexane/EtOAc (99:1 to 85:15) as an eluent. Colorless oil (951 mg, 35%). IR (neat) 634, 689, 1212, 1667, 1709, 2943, 3292 cm⁻¹; ¹H NMR (CDCl₃) δ 1.13–1.30 (m, 1H), 1.35–1.58 (m, 2H), 1.63–1.85 (m, 3H), 1.87 (t, *J* = 2.7 Hz, 1H), 1.92–2.34 (m, 6H), 2.39–2.48 (m, 1H), 2.87–2.96 (m, 1H), 7.38–7.45 (m, 2H), 7.50–7.57 (m, 1H), 7.83–7.88 (m, 2H). ¹³C NMR (CDCl₃) δ 18.58, 22.05, 22.56, 28.92, 34.32, 37.42, 42.83, 66.30, 68.63, 83.54, 128.70, 128.72, 133.08, 136.54, 197.75, 212.25. HRMS (ESI⁺) Calcd for C₁₈H₂₀O₂Na [M+Na]⁺: *m/z* 291.12555. Found: *m/z* 291.13521. *O*-Alkylation product **12** was also obtained as by-product (ca. 35%).

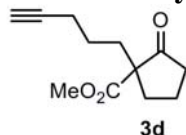


[2-(*tert*-Butyldimethylsiloxy)-1-(4-pentyn-1-yl)-2-cyclohexen-1-yl](phenyl)methanone (1c)



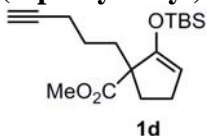
The compound **1c** was prepared according to the procedure for the preparation of **1a**, employing **3c** (674 mg, 2.51 mmol), Et₃N (0.525 mL, 3.77 mmol), TBSOTf (0.706 mL, 3.01 mmol) in CH₂Cl₂ (10 mL) and hexane/EtOAc (99.5:0.5 to 95:5) as an eluent. Colorless oil (861 mg, 90%). IR (neat) 832, 1174, 1249, 1655, 1680, 2930, 2950, 3311 cm⁻¹; ¹H NMR (CDCl₃) δ -0.05 (s, 3H), 0.12 (s, 3H), 0.65 (s, 9H), 1.55–1.81 (m, 5H), 1.90–2.09 (m, 3H), 2.11–2.31 (m, 5H), 4.89 (dd, *J* = 4.5, 3.6 Hz, 1H), 7.31–7.39 (m, 2H), 7.41–7.49 (m, 1H), 7.93–8.00 (m, 2H). ¹³C NMR (CDCl₃) δ -5.31, -5.22, 17.51, 18.63, 19.00, 23.64, 24.38, 25.09, 31.72, 35.92, 54.91, 68.08, 84.33, 101.95, 127.71, 128.48, 131.35, 137.72, 152.13, 203.49. HRMS (EI⁺) Calcd for C₂₄H₃₅O₂Si [M+H]⁺: *m/z* 383.24063. Found: *m/z* 383.24211.

Methyl 2-Oxo-1-(4-pentyn-1-yl)cyclopentanecarboxylate (3d)



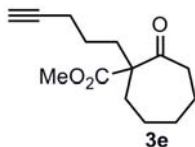
The compound **3d** was prepared according to the procedure for the preparation of **3a**, employing methyl 2-oxocyclopentanecarboxylate **9** (1.24 mL, 9.99 mmol), NaH (482 mg, 12.0 mmol) and 5-iodo-1-pentyne (2.15 g, 11.1 mmol). Purification by flash chromatography on silica gel (hexane/EtOAc 99:1 to 85:15) provided **3d** as a mixture of a trace amount of impurities. This mixture was used in the next step without further purification.

Methyl 2-(*tert*-Butyldimethylsiloxy)-1-(4-pentyn-1-yl)-2-cyclopentenecarboxylate (1d)



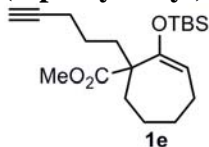
The compound **1d** was prepared according to the procedure for the preparation of **1a**, employing **3d** (a mixture of impurities, <9.99 mmol), Et₃N (2.03 mL, 14.6 mmol), TBSOTf (2.27 mL, 9.68 mmol) in CH₂Cl₂ (10 mL) and hexane/EtOAc (99.5:0.5 to 95:5) as an eluent. Colorless oil (2.14 g, 2 steps overall 96%). IR (neat) 781, 837, 854, 1251, 1647, 1730, 2858, 2931, 2951, 3313 cm⁻¹; ¹H NMR (CDCl₃) δ 0.16 (s, 3H), 0.20 (s, 3H), 0.94 (s, 9H), 1.46–1.61 (m, 2H), 1.70–1.96 (m, 3H), 1.98 (t, *J* = 2.7 Hz, 1H), 2.19–2.28 (m, 3H), 2.30–2.41 (m, 2H), 3.69 (s, 3H), 4.69 (br d, *J* = 2.4 Hz, 1H). ¹³C NMR (CDCl₃) δ -5.79, -5.12, 17.64, 18.65, 23.57, 25.21, 26.20, 31.53, 33.55, 51.44, 57.85, 68.22, 84.09, 102.23, 154.06, 175.66. HRMS (EI⁺) Calcd for C₁₈H₃₀O₃SiNa [M+Na]⁺: *m/z* 345.18564. Found: *m/z* 345.18531.

Methyl 2-Oxo-1-(4-pentyn-1-yl)cycloheptanecarboxylate (3e)



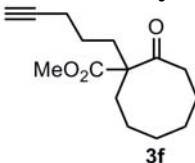
The compound **3e** was prepared according to the procedure for the preparation of **3a**, employing methyl 2-oxocycloheptanecarboxylate **10** (1.58 g, 10.0 mmol), NaH (482 mg, 12.1 mmol), 5-iodo-1-pentyne (2.15 g, 11.1 mmol) and hexane/EtOAc (99:1 to 85:15) as an eluent. Colorless oil (2.26 g, 96%). IR (neat) 631, 1150, 1168, 1224, 1701, 1732, 2962, 2934, 3286 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.40–1.82 (m, 10H), 1.95 (t, $J = 2.7$ Hz, 1H), 2.00–2.24 (m, 4H), 2.44–2.54 (m, 1H), 2.58–2.68 (m, 1H), 3.73 (s, 3H). ^{13}C NMR (CDCl_3) δ 18.52, 23.56, 24.59, 25.37, 29.66, 32.61, 34.33, 41.77, 52.01, 62.47, 68.54, 83.65, 172.90, 209.48. HRMS (ESI $^+$) Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: m/z 259.13047. Found: m/z 259.13016.

Methyl 2-(*tert*-Butyldimethylsiloxy)-1-(4-pentyn-1-yl)-2-cycloheptenecarboxylate (1e)



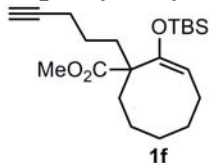
The compound **1e** was prepared according to the procedure for the preparation of **1a**, employing **3e** (958 mg, 4.06 mmol), Et_3N (1.70 mL, 12.2 mmol), TBSOTf (1.90 mL, 8.10 mmol) in CH_2Cl_2 (8.1 mL) and hexane/EtOAc/ Et_3N (99:0:1 to 95:4:1) as an eluent. Colorless oil (1.24 g, 87%). IR (neat) 776, 837, 1164, 1732, 2858, 2930, 2950, 3313 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.14 (s, 3H), 0.16 (s, 3H), 0.87 (s, 9H), 1.48–1.75 (m, 6H), 1.79–2.95 (m, 5H), 1.96–2.05 (m, 2H), 2.20 (td, $J = 7.2, 2.7$ Hz, 2H), 3.66 (s, 3H), 4.97 (dd, $J = 7.2, 5.7$ Hz, 1H). ^{13}C NMR (CDCl_3) δ -5.18, -4.70, 17.89, 18.87, 22.69, 23.47, 23.58, 25.50, 26.43, 31.35, 35.40, 51.38, 55.99, 68.20, 84.36, 108.47, 153.13, 175.54. HRMS (EI $^+$) Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M}+\text{Na}]^+$: m/z 373.21694. Found: m/z 373.21606.

Methyl 2-Oxo-1-(4-pentyn-1-yl)cyclooctanecarboxylate (3f)



The compound **3f** was prepared according to the procedure for the preparation of **3a**, employing methyl 2-oxocyclooctanecarboxylate **11**³ (1.47 g, 8.03 mmol), NaH (386 mg, 9.64 mmol), 5-iodo-1-pentyne (1.87 g, 9.64 mmol) and hexane/EtOAc (99:1 to 85:15) as an eluent. Colorless oil (1.81 g, 90%). IR (neat) 631, 1077, 1166, 1219, 1704, 2858, 2930, 3287 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.90–1.05 (m, 1H), 1.26–1.90 (m, 9H), 1.95 (t, $J = 2.7$ Hz, 1H), 1.97–2.32 (m, 6H), 2.43–2.55 (m, 1H), 2.71 (td, $J = 12.0, 3.9$ Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (CDCl_3) δ 18.51, 22.87, 23.61, 23.90, 25.23, 28.13, 29.03, 29.88, 38.28, 52.12, 61.82, 68.46, 83.67, 172.19, 212.25. Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3$: C, 71.97; H, 8.86%. Found: C, 71.69; H, 8.90%.

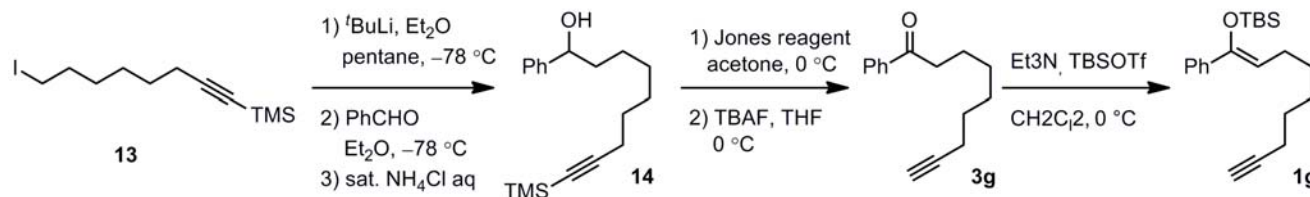
Methyl 2-(*tert*-Butyldimethylsiloxy)-1-(4-pentyn-1-yl)-2-cyclooctenecarboxylate (1f)



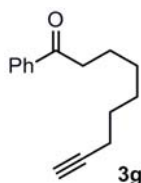
The compound **1f** was prepared according to the procedure for the preparation of **1a**, employing **3f** (785 mg, 3.13 mmol), Et_3N (1.31 mL, 9.40 mmol), TBSOTf (1.47, 3.01 mmol) in CH_2Cl_2 (10 mL) and

hexane/EtOAc (99.5:0.5 to 95:5) as an eluent. Colorless oil (861 mg, 90%). IR (neat) 627, 776, 837, 1146, 1648, 1731, 2929, 2950, 3313 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.18 (s, 6H), 0.88 (s, 9H), 1.32–1.45 (m, 1H), 1.46–1.67 (m, 6H), 1.73–2.03 (m, 5H), 1.93 (t, J = 2.7 Hz, 1H), 2.13–2.42 (m, 2H), 2.18 (td, J = 7.8, 2.7 Hz, 2H), 3.67 (s, 3H), 4.75 (dd, J = 11.5, 9.3 Hz, 1H). ^{13}C NMR (CDCl_3) δ –5.15, –5.55, 17.92, 18.79, 22.94, 23.10, 23.41, 25.40, 25.59, 27.36, 34.13, 36.79, 51.24, 56.23, 68.23, 84.35, 104.81, 152.01, 175.55. Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{O}_3\text{Si}$: C, 69.18; H, 9.95%. Found: C, 68.83; H, 10.02%.

Scheme 2. Preparation of **1g**.⁴



1-Phenyl-8-nonyn-1-one (**3g**)

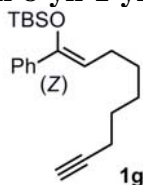


To a solution of the 8-iodo-1-(trimethylsilyl)-1-octyne (**13**)⁵ (1.96 g 6.35 mmol) in pentane/ Et_2O (3:2, 60 mL) was added dropwise $t\text{BuLi}$ (7.98 mL of 1.59 M in Et_2O , 12.7 mmol) at -78°C under Ar atmosphere. The reaction mixture was stirred at this temperature for 20 min. Then a solution of benzaldehyde (656 mg, 6.15 mmol) in Et_2O (6 mL) was added and the mixture was stirred at -78°C for 1 h before being quenched with saturated aqueous NH_4Cl . The organic layer was washed with water (2×50 mL) and brine (50 mL), and separated. The combined aqueous layer was extracted with ether (3×50 mL). The organic layers were combined, dried over MgSO_4 , filtered and concentrated under reduced pressure to afford **14** as a crude product. This crude product was used in the next step without further purification.

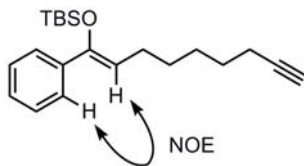
To a solution of **14** (6.15 mmol) in acetone (25 mL), Jones reagent (6.50 mL of 1.00 M in H_2SO_4 and H_2O , 6.50 mmol) was added dropwise at 0°C under air and a mixture was stirred at this temperature for 15 min. Then MeOH (5 mL) was added at 0°C , and the precipitates were filtered off and washed with Et_2O (30 mL). The filtrate was washed with brine (2×50 mL) and 15% NaOH (50 mL), and separated. The combined aqueous layer was extracted with ether (3×50 mL). The organic layers were combined, dried over MgSO_4 , filtered and concentrated under reduced pressure to afford 1-phenyl-9-(trimethylsilyl)-8-nonyn-1-one as a crude product.

To a solution of this crude product (895 mg, 3.12 mmol) in THF (6.2 mL), TBAF (3.44 mL of 1.0 M in THF, 3.44 mL) was added at 0°C . After stirring at this temperature for 6 h, the reaction mixture was diluted with water (10 mL) and Et_2O (10 mL). The organic layer was washed with water (3×10 mL), and separated. The combined aqueous layer was extracted with ether (3×10 mL). The organic layers were combined, dried over MgSO_4 , filtered and concentrated under reduced pressure to afford **3g** as a crude product. The residue was purified by flash chromatography on silica gel (hexane/ EtOAc 99:1 to 95:5) to afford **3g** as a white solid (466 mg, 3 steps overall 35%). IR (neat) 624, 688, 1266, 1447, 1679, 2859, 2932, 3289, 3306 cm^{-1} ; Mp $31.5\text{--}33.6^\circ\text{C}$. ^1H NMR (CDCl_3) δ 1.35–1.62 (m, 6H), 1.76 (quint, J = 7.2 Hz, 2H), 1.94 (t, J = 2.4 Hz, 1H), 2.20 (td, J = 6.9, 2.4 Hz, 2H), 2.98 (t, J = 7.2 Hz, 2H), 7.43–7.50 (m, 2H), 7.53–7.60 (m, 1H), 7.94–7.99 (m, 2H). ^{13}C NMR (CDCl_3) δ 17.95, 23.73, 27.91, 28.18, 28.41, 38.06, 68.10, 84.24, 127.83, 128.37, 132.71, 136.85, 200.11. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$: C, 84.07; H, 8.47%. Found: C, 83.72; H, 8.48%.

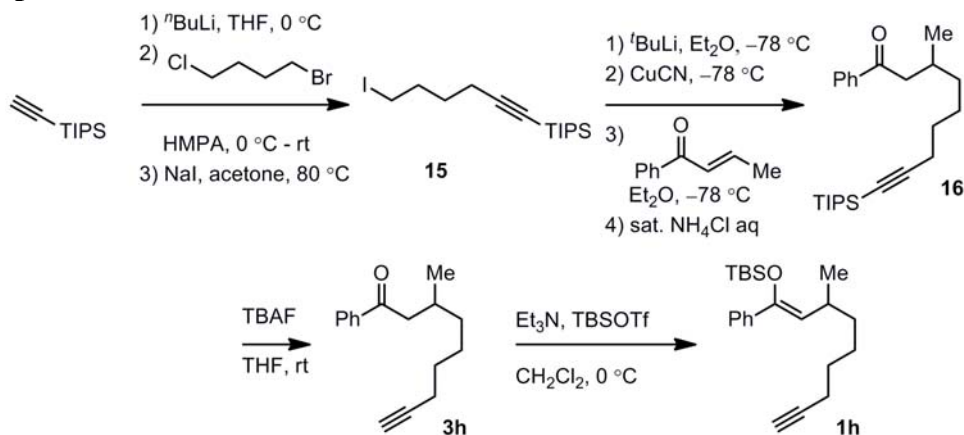
(Z)-tert-Butyldimethyl[(1-phenyl-1-nonen-8-yn-1-yl)oxy]silane (1g) (*E/Z* = 14/86)



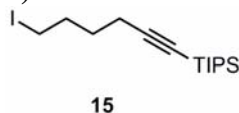
The compound **1g** was prepared according to the procedure for the preparation of **1a**, employing **3g** (446 mg, 2.09 mmol), Et₃N (0.873 mL, 4.18 mmol), TBSOTf (0.980 mL, 4.18 mmol) in CH₂Cl₂ (4.1 mL) and hexane/EtOAc (99.5/0.5 to 95/5) as the eluent. Colorless oil (651 mg, 95%, *E/Z* = 14/86). IR (neat) 626, 696, 765, 778, 836, 1063, 1253, 2857, 2930, 3312 cm⁻¹; ¹H NMR of (*E*)-**1g** (CDCl₃) δ 0.06 (s, 0.86×6H), 0.03 (s, 0.14×6H), 0.91 (s, 0.14×9H), 0.98 (s, 0.86×9H), 1.35–1.55 (m, 6H), 1.93 (m, 0.14×1H), 1.94 (t, *J* = 2.7 Hz, 0.86×1H), 2.05–2.24 (m, 6H), 5.01 (t, *J* = 7.2 Hz, 0.14×1H), 5.10 (t, *J* = 7.2 Hz, 0.86×1H), 7.19–7.37 (m, 3H), 7.40–7.45 (m, 2H). ¹³C NMR of (CDCl₃) δ -4.24 (0.86×1C), -4.71 (0.14×1C), 17.97 (0.14×1C), 18.13 (0.86×1C), 18.15 (0.14×1C), 18.20 (0.86×1C), 25.61 (0.14×1C), 25.73 (0.86×1C), 25.86 (0.86×1C), 27.28 (0.14×1C), 28.13 (0.14×1C), 28.23 (0.86×1C), 28.42 (0.86×1C), 29.02 (0.86×1C), 30.09 (0.14×1C), 68.16 (0.14×1C), 68.16 (1C), 84.38 (0.14×1C), 84.43 (0.86×1C), 110.96 (0.14×1C), 111.64 (0.86×1C), 125.87 (0.86×1C), 127.36 (0.86×1C), 127.60 (0.14×1C), 127.74 (0.14×1C), 127.88 (0.86×1C), 128.32 (0.14×1C), 137.93 (0.14×1C), 139.83 (0.86×1C), 149.44 (0.86×1C), 149.55 (0.14×1C). Another one peak of *E*-isomer was probably overlapped with that of *Z*-isomer. HRMS (APCI⁺) Calcd for C₂₁H₃₃OSi [M+H]⁺: *m/z* 329.22952. Found: *m/z* 329.22888. The geometry of major *Z*-isomer was confirmed by an NOE experiment as shown below.



Scheme 3. Preparation of 1h.



6-iodo-1-triisopropylsilyl-1-hexyne (15)

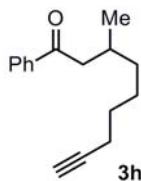


To a solution of triisopropylsilylacetylene (3.55 g, 19.5 mmol) in THF (40 mL) was added *n*-BuLi (11.6 mL of 1.67 M in hexane, 19.4 mL) at 0 °C, and the mixture was stirred at this temperature for 1 h. Then 1-bromo-4-chloro-butane (3.16 g, 18.2 mmol) and HMPA (3.38 mL, 19.4 mmol) was added at 0 °C, and the reaction mixture was allowed to warm to room temperature and stirred for 15 h. The

resulting mixture was treated with saturated aqueous NH_4Cl (30 mL) and hexane (30 mL), and the aqueous layer was separated. The organic layer was washed with water (30 mL) and brine (30 mL), and separated. The combined aqueous layer was extracted with hexane (3×30 mL). The organic layers were combined, dried over MgSO_4 , filtered and concentrated under reduced pressure to afford the 6-chloro-1-triisopropylsilyl-1-hexyne as a crude product (pale yellow oil, 4.99 g). This crude product was used in the next step without further purification.

To a solution of 6-chloro-1-triisopropylsilyl-1-hexyne (4.99 g) in acetone (100 mL), NaI (14.6 g, 96.9 mmol) was added, and the mixture was stirred at 80 °C overnight. The resulting orange suspension was cooled to rt, solvent was removed by an evaporator, and saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ (50 mL) and hexane (100 mL) was added. The organic layer was washed with water (2×50 mL) and brine (50 mL), and separated. The combined aqueous layer was extracted with hexane (3×50 mL). The organic layer was combined, dried over MgSO_4 , filtered and concentrated under reduced pressure. Flash silica gel column purification (hexane) of the crude product afforded **15** as a colorless oil (5.58 g, 2 steps overall 84%). IR (neat) 659, 674, 882, 1462, 2171, 2863, 2941 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.00–1.10 (m, 21H), 1.65 (quint., $J = 7.2$ Hz, 2H), 1.98 (quint., $J = 7.2$ Hz, 2H), 2.30 (t, $J = 6.9$ Hz, 2H), 3.23 (t, $J = 6.9$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 6.04, 11.10, 18.49, 18.60, 29.21, 32.12, 80.99, 107.92. HRMS (EI^+) Calcd for $\text{C}_{15}\text{H}_{29}\text{Si}$ [$\text{M}]^+$: m/z 364.10832. Found: m/z 364.10752.

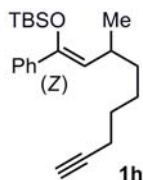
3-Methyl-1-phenyl-8-nonyn-1-one (3h)



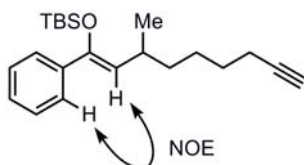
To a solution of **15** (4.64 g, 12.7 mmol) in Et_2O (120 mL) was added $t\text{BuLi}$ (16.3 mL of 1.55 M in pentane, 25.3 mmol) at -78 °C, and the mixture was stirred for 40 min. Then, CuCN (533 mg, 6.36 mmol) was added one portion to a mixture, and the pale yellow suspension was stirred at -78 °C for additional 15 min. To this suspension, a solution of (*E*)-1-phenyl-2-buten-1-one (888 mg, 6.07 mmol) was added dropwise at -78 °C over 7 min. The resulting dark red solution was quenched with saturated aqueous NH_4Cl (120 mL) after being stirred for 20 min (the consumption of SM was checked by TLC), and a mixture was stirred until the color of organic phase turned to blue. The organic phase was washed with saturated aqueous NH_4Cl (5×100 mL), and separated, dried over MgSO_4 , filtered and concentrated under reduced pressure to afford the 1,4-adduct **16** as a crude product (yellow oil, 3.51 g.). The residue was purified by flash chromatography on silica gel (hexane/ EtOAc 99.5:0.5 to 97:3) to afford **16** as a colorless oil (611 mg, 26%).

To a solution of **16** (611 mg, 1.59 mmol) in THF (8.0 mL), TBAF (2.38 mL of 1.0 M in THF, 2.38 mL) was added at 0 °C. After stirring at room temperature for 13 h, the reaction mixture was diluted with water (10 mL) and Et_2O (5 mL). The organic layer was washed with water (3×10 mL), and separated. The combined aqueous layer was extracted with ether (3×10 mL). The organic layers were combined, dried over MgSO_4 , filtered and concentrated under reduced pressure to afford **3h** as a crude product. The residue was purified by flash chromatography on silica gel (hexane/ EtOAc 99:1 to 96:4) to afford **3h** as a colorless oil (272 mg, 75%). IR (neat) 631, 690, 751, 1213, 1448, 1682, 2861, 2934, 3301 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.97 (d, $J = 6.9$ Hz, 3 H), 1.20–1.58 (m, 6H), 1.94 (t, $J = 2.7$ Hz, 1H), 2.11–2.23 (m, 3H), 2.77 (dd, $J = 15.8, 6.0$ Hz, 1H), 2.95 (dd, $J = 15.8, 6.0$ Hz, 1H), 7.43–7.50 (m, 2H), 7.53–7.60 (m, 1H), 7.93–7.98 (m, 2H). ^{13}C NMR (CDCl_3) δ 18.05, 19.69, 25.81, 28.23, 29.30, 36.20, 45.62, 68.16, 84.32, 127.99, 128.47, 132.79, 137.33, 200.21. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: C, 84.16; H, 8.83%. Found: C, 83.96; H, 8.90%.

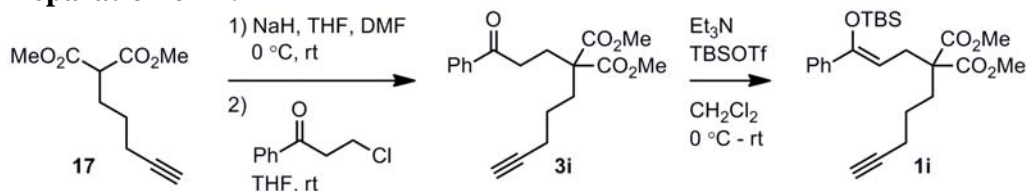
(*Z*)-*tert*-Butyldimethyl[(3-methyl-1-phenyl-1-nonen-8-yn-1-yl)oxy]silane (1h) (*E/Z* = 13/87)



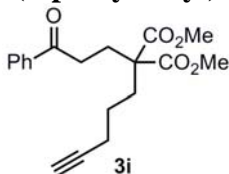
The compound **1h** was prepared according to the procedure for the preparation of **1a**, employing **3h** (257 mg, 1.13 mmol), Et₃N (0.235 mL, 1.69 mmol), TBSOTf (0.317 mL, 1.35 mmol) in CH₂Cl₂ (5.6 mL) and hexane/EtOAc (99.5:0.5 to 97:3) as an eluent. Colorless oil (342 mg, 89%, *E/Z* = 13/87). IR (neat) 626, 697, 764, 778, 836, 1062, 1255, 1647, 2858, 2930, 2954, 3313 cm⁻¹; ¹H NMR of (*Z*)-**1h** (CDCl₃) δ -0.10 (s, 3H), -0.03 (s, 3H), 0.98 (s, 9H), 1.01 (d, *J* = 6.6 Hz, 3 H), 1.24–1.58 (m, 6H), 1.93 (t, *J* = 2.7 Hz, 1H), 2.18 (td, *J* = 6.9, 2.7 Hz, 2H), 2.62–2.74 (m, 1H), 4.85 (d, *J* = 9.6 Hz, 1H), 7.17–7.36 (m, 3H), 7.39–7.45 (m, 2H). [(*E*)-**1h**: 4.79 (d, *J* = 10.8 Hz, 1H)]. ¹³C NMR of (*Z*)-**1h** (CDCl₃) δ -4.28, -4.11, 18.13, 18.27, 20.82, 25.80, 26.53, 28.54, 30.08, 37.07, 68.13, 84.48, 118.23, 126.18, 127.40, 127.86, 140.01, 148.62. Anal. Calcd for C₂₂H₂₄OSi: C, 77.13; H, 10.00%. Found: C, 76.74; H, 10.04%. The geometry of major *Z*-isomer was confirmed by an NOE experiment as shown below.



Scheme 4. Preparation of **1i**.

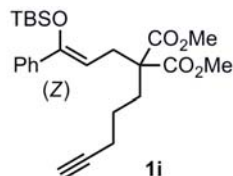


Dimethyl 2-(3-Oxo-3-phenylpropyl)-2-(4-pentyn-1-yl)malonate (**3i**)

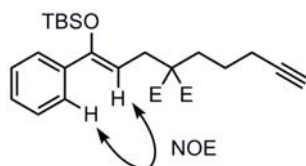


The compound **3i** was prepared according to the procedure for the preparation of **3a**, employing dimethyl 2-(4-pentyn-1-yl)malonate (**17**) (1.13 g, 5.04 mmol), NaH (241 mg, 6.00 mmol), 3-chloro-1-phenyl-1-propanone (1.05 g, 5.99 mmol), NaI (75.1 mg, 0.500 mmol) at 80 °C (reflux) for 11 h. Purification by silica gel chromatography (hexane/EtOAc 95:5 to 80:20) afforded **3i** as a colorless oil (1.17 g, 70%). IR (neat) 689, 1173, 1434, 1448, 1683, 1727, 2953, 3288 cm⁻¹; ¹H NMR (CDCl₃) δ 1.42–1.54 (m, 2H), 1.96 (t, *J* = 2.4 Hz, 1H), 2.03–2.11 (td, *J* = 6.9, 2.4 Hz, 2H), 2.31–2.38 (m, 2H), 2.96–3.03 (m, 2H), 3.74 (s, 6H), 7.44–7.51 (m, 2H), 7.54–7.61 (m, 1H), 7.93–7.98 (m, 2H). ¹³C NMR (CDCl₃) δ 18.43, 23.18, 27.13, 32.73, 33.59, 52.41, 56.66, 68.85, 83.48, 128.06, 128.63, 133.18, 136.68, 171.82, 198.92. HRMS (ESI⁺) Calcd for C₁₉H₂₂O₅Na [M+Na]⁺: *m/z* 353.13594. Found: *m/z* 353.13528.

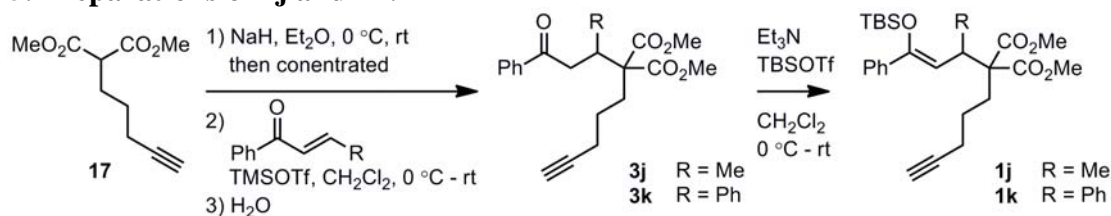
(*Z*)-Dimethyl 2-[3-(*tert*-Butyldimethylsiloxy)-3-phenylallyl]-2-(4-pentyn-1-yl)malonate (**1i**) (*E/Z* = 10/90)



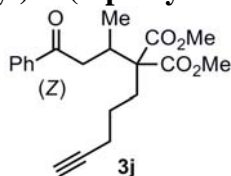
The compound **1i** was prepared according to the procedure for the preparation of **1a**, employing **3i** (609 mg, 1.84 mmol), Et₃N (0.770 mL, 5.53 mmol), TBSOTf (0.864 mL, 3.68 mmol) in CH₂Cl₂ (3.7 mL) and hexane/EtOAc (99:1 to 87:13) as an eluent. Colorless oil (781 mg, 87%, *E/Z* = 10/90). IR (neat) 760, 779, 837, 1074, 1254, 1732, 2931, 2953, 2931, 2953, 3308 cm⁻¹; ¹H NMR of (*Z*)-**1i** (CDCl₃) δ -0.06 (s, 3H), 0.99 (s, 9H), 1.42–1.57 (m, 2H), 1.91 (t, *J* = 2.7 Hz, 1H), 1.95–2.02 (m, 2H), 2.18 (td, *J* = 7.2, 2.7 Hz, 2H), 2.84 (d, *J* = 7.5 Hz, 1H), 4.89 (d, *J* = 7.5 Hz, 1H), 7.23–7.31 (m, 3H), 7.36–7.41 (m, 2H). [(*E*)-**1i**: 2.74 (d, *J* = 7.8 Hz, 2H), 4.77 (t, *J* = 7.8 Hz, 1H)]. ¹³C NMR of (*Z*)-**1i** (CDCl₃) δ -4.28, -4.11, 18.13, 18.27, 20.82, 25.80, 26.53, 28.54, 30.08, 37.07, 68.13, 84.48, 118.23, 126.18, 127.40, 127.86, 140.01, 148.62. Anal. Calcd for C₂₅H₃₆OSi: C, 67.53; H, 8.16%. Found: C, 67.29; H, 8.25%. The geometry of major *Z*-isomer was confirmed by an NOE experiment as shown below.



Scheme 5. Preparations of **1j** and **1k**.⁴



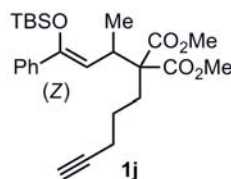
Dimethyl 2-(4-Oxo-4-phenyl-2-butanyl)-2-(4-pentyn-1-yl)malonate (**3j**)



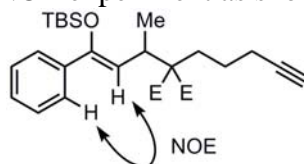
To a suspension of NaH (0.224 g, 5.59 mmol) in Et₂O (4.6 mL) was added a solution of **17** (1.04 g, 4.59 mmol) in Et₂O (9.2 mL) at 0 °C under Ar atmosphere. After stirring for 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Then, the mixture was concentrated *in vacuo* to remove the solvent, and the reaction vessel was charged with Ar. To the reaction vessel, CH₂Cl₂ (23 mL), (*E*)-1-phenyl-2-buten-1-one (673 mg, 4.61 mmol) and TMSOTf (1.69 mL, 9.17 mmol) was added in this order at 0 °C, and the mixture was stirred at this temperature for 10 h. The resulting trimethylsilyl enol ether was hydrolyzed with aq NaHCO₃ to **3j**. The organic layer was washed with H₂O (3 × 10 mL) and separated. The combined aqueous layer was extracted with Et₂O (3 × 10 mL). The organic layers were combined, dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc 95:5 to 80:20) to give **3j** as a colorless oil (1.17 g, 74%). IR (neat) 776, 835, 1186, 1252, 1712, 2933, 2954, 3288 cm⁻¹; ¹H NMR (CDCl₃) δ 0.97 (d, *J* = 6.9 Hz, 3H), 1.42–1.59 (m, 2H), 1.96 (t, *J* = 2.7 Hz, 1H), 2.03–2.11 (m, 2H), 2.21 (td, *J* = 7.2, 2.7 Hz, 2H), 2.82 (dd, *J* = 16.5, 10.5 Hz, 1H), 2.91–3.04 (m, 1H), 3.30 (d, *J* = 16.5 Hz, 1H), 3.75 (s, 3H), 3.79 (s, 3H), 7.43–7.51 (m, 2H), 7.54–7.60 (m, 2H), 7.97–8.03 (m, 2H). ¹³C NMR (CDCl₃) δ 15.26, 18.35, 23.41, 32.41, 32.58, 42.28,

51.93, 52.02, 61.07, 68.76, 83.33, 128.02, 128.46, 132.95, 136.90, 171.00, 171.55, 198.87. HRMS (ESI⁺) Calcd for C₂₀H₂₄O₅Na [M+Na]⁺: *m/z* 367.15160. Found: *m/z* 367.15084.

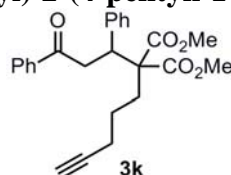
(Z)-Dimethyl 2-[4-(*tert*-Butyldimethylsiloxy)-4-phenyl-3-buten-2-yl]-2-(4-pentyn-1-yl)malonate (1j)



The compound **1j** was prepared according to the procedure for the preparation of **1a**, employing **3j** (996 mg, 2.89 mmol), Et₃N (1.21 mL, 8.68 mmol), TBSOTf (1.36 mL, 5.80 mmol) in CH₂Cl₂ (5.8 mL) and hexane/EtOAc (99:1 to 92:8) as the eluent. The further purification was conducted by GPC. Colorless oil (871 mg, 66%). IR (neat) 698, 766, 779, 838, 1062, 1252, 1646, 1727, 2932, 2953, 3310 cm⁻¹; ¹H NMR (CDCl₃) δ -0.15 (s, 3H), 0.01 (s, 3H), 1.00 (s, 9H), 1.12 (d, *J* = 6.9 Hz, 3 H), 1.32–1.50 (m, 1H), 1.62–1.78 (m, 1H), 1.90 (t, *J* = 2.7 Hz, 1H), 1.94–2.02 (m, 2H), 2.16 (td, *J* = 6.9, 2.7 Hz, 2H), 3.49 (dq, *J* = 10.5, 6.9 Hz, 1H), 3.72 (s, 3H), 3.75 (s, 3H), 4.95 (d, *J* = 10.5 Hz, 1H), 7.24–7.32 (m, 3H), 7.35–7.41 (m, 2H). ¹³C NMR (CDCl₃) δ -4.49, -4.08, 17.42, 17.99, 18.60, 23.63, 25.61, 33.93, 34.50, 51.56, 51.83, 61.47, 68.44, 83.63, 111.87, 126.44, 127.76, 127.82, 139.51, 150.51, 171.22, 171.64. HRMS (ESI⁺) Calcd for C₂₆H₃₈O₅SiNa [M+Na]⁺: *m/z* 481.23807. Found: *m/z* 481.23699. The geometry of major *Z*-isomer was confirmed by an NOE experiment as shown below.

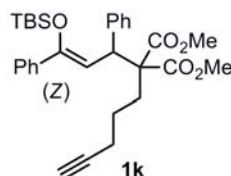


Dimethyl 2-(3-Oxo-1,3-diphenylpropyl)-2-(4-pentyn-1-yl)malonate (3k)

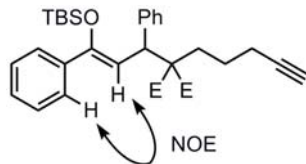


The compound **3k** was prepared according to the procedure for the preparation of **3j**, employing **17** (896 mg, 4.00 mmol), NaH (193 mL, 4.83 mmol), (*E*)-chalcone (836 mg, 4.01 mmol), TMSOTf (1.17 mL, 5.99 mmol) and hexane/EtOAc (90:10 to 80:20) as an eluent. Colorless viscous oil (1.29 g, 79%). IR (neat) 690, 702, 749, 1170, 1213, 1433, 1448, 1597, 1685, 1726, 2951, 3288 cm⁻¹; ¹H NMR (CDCl₃) δ 1.40–1.69 (m, 2H), 1.73 (dd, *J* = 4.8, 12.0 Hz, 1H), 1.84 (dd, *J* = 8.1, 12.0 Hz, 1H), 3.75 (s, 3H), 3.78 (dd, *J* = 17.4 Hz, 10.5 Hz, 1H), 3.80 (s, 3H), 4.17 (dd, *J* = 10.5, 2.7 Hz, 1H), 7.11–7.17 (m, 2H), 7.17–7.26 (m, 3H), 7.38–7.45 (m, 2H), 7.48–7.55 (m, 2H). ¹³C NMR (CDCl₃) δ 18.49, 23.89, 33.65, 41.99, 44.75, 52.18, 52.47, 61.74, 68.69, 83.54, 127.46, 128.13, 128.35, 128.54, 129.08, 132.99, 137.02, 138.94, 171.17, 171.65, 197.96. Anal. Calcd for C₂₅H₂₆O₅: C, 73.87; H, 6.45%. Found: C, 73.49; H, 6.57%.

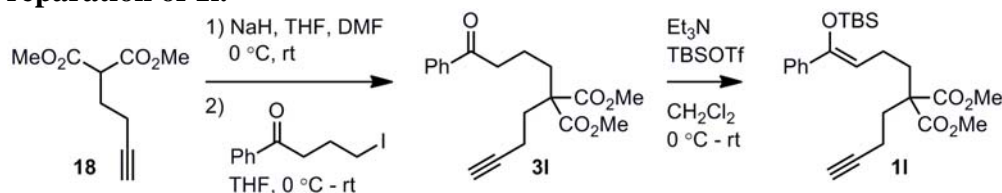
(Z)-Dimethyl 2-[3-(*tert*-Butyldimethylsiloxy)-1,3-diphenylallyl]-2-(4-pentyn-1-yl)malonate (1k) (*E/Z* = 4/96)



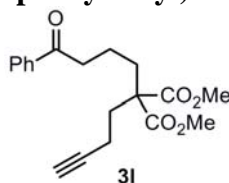
The compound **1k** was prepared according to the procedure for the preparation of **1a**, employing **3k** (1.02 g, 2.50 mmol), Et₃N (1.05 mL, 7.53 mmol), TBSOTf (1.17 mL, 4.99 mmol) in CH₂Cl₂ (5.0 mL) and hexane/EtOAc (99.5:0.5 to 97:3) as an eluent. White solid (1.26 mg, 97%, *E/Z* 4:96). IR (neat) 700, 769, 780, 1648, 1722, 1751, 2933, 2954, 3277 cm⁻¹; Mp: 71.9–73.0 °C. ¹H NMR of (*Z*)-**1k** (CDCl₃) δ –0.28 (s, 3H), –0.25 (s, 3H), 0.99 (s, 9H), 1.24–1.43 (m, 1H), 1.60–1.76 (m, 1H), 1.90 (t, *J* = 2.7 Hz, 1H), 1.92–2.11 (m, 2H), 2.15 (br t, *J* = 6.0 Hz, 2H), 3.57 (s, 3H), 3.66 (s, 3H), 4.68 (d, *J* = 10.8 Hz, 1H), 5.68 (d, *J* = 10.8 Hz, 1H), 7.15–7.34 (m, 8H), 7.36–7.42 (m, 2H). [(*E*)-**1k**: δ –0.14 (s, 3H), –0.10 (s, 3H), 1.02 (s, 9H), 5.35 (d, *J* = 10.2 Hz, 1H)]. ¹³C NMR of (*Z*)-**1j** (CDCl₃) δ –4.60, –3.79, 18.12, 18.70, 23.89, 25.75, 34.37, 45.22, 51.72, 51.92, 63.24, 68.48, 83.79, 109.52, 126.80, 127.79, 127.95, 128.01, 129.49, 139.75, 140.51, 150.94, 171.00, 171.12. Anal. Calcd for C₃₁H₄₀O₅Si: C, 71.50; H, 7.74%. Found: C, 71.34; H, 7.78%. The geometry of major *Z*-isomer was confirmed by an NOE experiment as shown below.



Scheme 6. Preparation of **1l**.

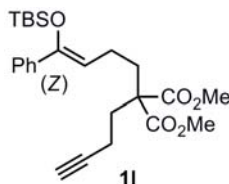


Dimethyl 2-(3-Butyn-1-yl)-2-(4-Oxo-4-phenylbutyl)malonate (**3l**)



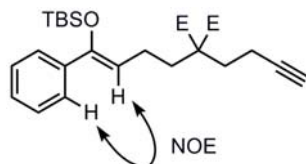
The compound **3l** was prepared according to the procedure for the preparation of **3a**, employing dimethyl 2-(3-butyn-1-yl)malonate (**18**) (1.04 g, 5.01 mmol), NaH (240 mg, 6.00 mmol), 4-iodo-1-phenyl-1-butanone⁶ (1.65 g, 6.02 mmol) at room temperature overnight. Purification by silica gel chromatography (hexane/EtOAc 95:5 to 75:25) afforded **3l** as a colorless oil (0.951 g, 57%). IR (neat) 690, 1175, 1199, 1434, 1448, 1683, 1728, 2953, 3289 cm⁻¹; ¹H NMR (CDCl₃) δ 1.57–1.70 (m, 2H), 1.96–2.06 (m, 3H), 2.21–2.24 (m, 4H), 3.01 (t, *J* = 6.9 Hz, 2H), 3.75 (s, 6H), 7.43–7.50 (m, 2H), 7.54–7.60 (m, 1H), 7.93–7.97 (m, 2H). ¹³C NMR (CDCl₃) δ 13.42, 18.07, 30.88, 31.60, 37.71, 52.11, 56.57, 68.65, 82.83, 127.68, 128.36, 132.83, 136.58, 171.22, 198.98. HRMS (ESI⁺) Calcd for C₁₉H₂₂O₅Na [M+Na]⁺: *m/z* 353.135894. Found: *m/z* 353.13539.

(*Z*)-Dimethyl 2-(3-butyn-1-yl)-2-[4-(*tert*-butyldimethylsiloxy)-4-phenyl-3-buten-1-yl]malonate (**1l**) (*E/Z* = 19/81)

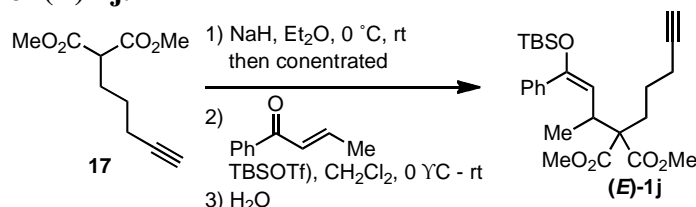


The compound **1l** was prepared according to the procedure for the preparation of **1a**, employing **3l** (724 mg, 2.19 mmol), Et₃N (0.458 mL, 3.29 mmol), TBSOTf (0.617 mL, 2.63 mmol) in CH₂Cl₂ (8.8 mL) and hexanes/EtOAc (99/1 to 92/8) as an eluent. Colorless oil (794 mg, 81%, *E/Z* = 19/81). IR

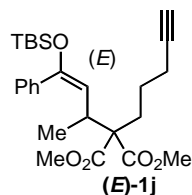
(neat) 697, 758, 779, 838, 1176, 1196, 1253, 1732, 2931, 2954, 3308 cm^{-1} ; ^1H NMR of (**Z**)-**11** (CDCl_3) δ -0.11 (s, 6H), 0.97 (s, 9H), 1.91–2.28 (m, 9H), 3.71 (s, 6H), 4.93–5.05 (m, 1H), 7.19–7.44 (m, 5H). ^{13}C NMR of (**Z**)-**11** (CDCl_3) δ -4.36, 13.76, 18.00, 20.82, 25.61, 31.04, 32.21, 52.21, 56.60, 68.72, 82.92, 109.88, 125.80, 127.54, 127.86, 139.36, 150.08, 171.47. HRMS (ESI^+) Calcd for $\text{C}_{25}\text{H}_{36}\text{O}_5\text{SiNa}$ $[\text{M}+\text{Na}]^+$: m/z 467.22169. Found: m/z 467.22242. The geometry of major Z-isomer was confirmed by NOE experiment as shown below.



Scheme 7. Preparation of (**E**)-**1j**.⁴

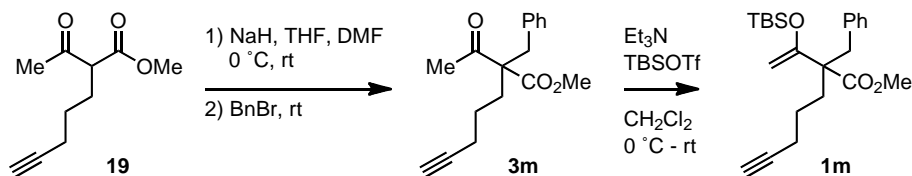


(**E**)-Dimethyl 2-[4-(*tert*-Butyldimethylsiloxy)-4-phenyl-3-buten-2-yl]-2-(4-pentyn-1-yl)malonate [(**E**)-**1j**] (**E**/**Z** = 86/14)

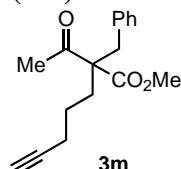


To a suspension of NaH (149 mg, 3.73 mmol) in Et_2O (3 mL) was added a solution of **17** (679 mg, 3.04 mmol) in Et_2O (6 mL) at 0 °C under Ar atmosphere. After stirring for 10 min, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. Then, the mixture was concentrated *in vacuo* to remove the solvent, and the reaction vessel was charged with Ar. To the reaction vessel, CH_2Cl_2 (23 mL), (**E**)-1-phenyl-2-buten-1-one (452 mg, 3.09 mmol) and TBSOTf (1.07 mL, 4.56 mmol) was added in this order at -78 °C, and the mixture was allowed to slowly warm to room temperature with stirring for 24 h. The resulting trimethylsilyl enol ether was hydrolyzed with aq NaHCO_3 to **3j**. The organic layer was washed with H_2O (3 \times 10 mL), and separated. The combined aqueous layer was extracted with Et_2O (3 \times 10 mL). The organic layers were combined, dried over MgSO_4 , filtered and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane/ EtOAc 99.5:0.5 to 92:8) and GPC to give (**E**)-**1j** as a colorless oil (735 g, 53%). IR (neat) 699, 778, 836, 1252, 1646, 1728, 2931, 2953, 3310 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.05 (s, 3H), 0.08 (s, 3H), 0.88 (s, 9H), 1.04–1.22 (m, 2H), 1.15 (d, J = 6.9 Hz, 3H), 1.75–1.91 (m, 2H), 1.90 (t, J = 2.7 Hz, 1H), 2.04 (td, J = 7.2, 2.7 Hz, 2H), 2.96–3.08 (m, 1H), 3.68 (s, 3H), 3.71 (s, 3H), 4.90 (d, J = 11.4 Hz, 1H), 7.22–7.38 (m, 5H). ^{13}C NMR (CDCl_3) δ -4.82, -4.49, 17.96, 18.51, 18.62, 23.49, 25.55, 33.87, 36.34, 51.74, 51.91, 61.64, 68.45, 83.63, 110.56, 128.01, 128.05, 128.07, 137.75, 151.25, 171.16, 171.47. HRMS (ESI^+) Calcd for $\text{C}_{26}\text{H}_{38}\text{O}_5\text{SiNa}$ $[\text{M}+\text{Na}]^+$: m/z 481.23807. Found: m/z 481.23733.

Scheme 8. Preparation of **1m**.

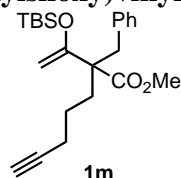


Methyl 2-Acetyl-2-benzyl-6-heptynoate (3m)



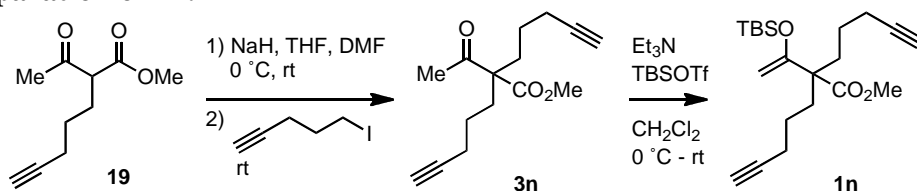
The compound **3m** was prepared according to the procedure for the preparation of **3a**, employing methyl 2-acetyl-6-heptynoate (**19**) (729 mg, 4.00 mmol), NaH (192 mg, 4.80 mmol), benzyl bromide (0.582 mL, 4.80 mmol) at room temperature for 20 min. Purification by silica gel chromatography (hexane/EtOAc 99:1 to 85:15) afforded **3m** as a colorless oil (0.834 g, 88%). IR (neat) 635, 701, 1176, 1433, 1455, 1709, 1742, 2952, 3289 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.23–1.45 (m, 1H), 1.45–1.61 (m, 1H), 1.87–1.97 (m, 2H), 1.96 (t, $J = 2.7$ Hz, 1H), 2.12 (s, 3H), 2.15–2.23 (m, 2H), 3.12 (d, $J = 14.4$, 1H), 3.23 (d, $J = 14.4$, 1H), 3.72 (s, 3H), 7.02–7.07 (m, 2H), 7.18–7.28 (m, 3H). ^{13}C NMR (CDCl_3) δ 18.27, 22.82, 26.89, 30.15, 37.08, 51.96, 64.32, 68.92, 83.25, 126.81, 128.22, 129.67, 136.05, 172.17, 204.60. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$: C, 74.97; H, 7.40%. Found: C, 74.74; H, 7.43%.

Methyl 2-Benzyl-2-[1-(*tert*-butyldimethylsiloxy)vinyl]-6-heptynoate (1m)

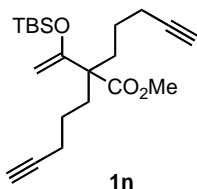


The compound **1m** was prepared according to the procedure for the preparation of **1a**, employing **3m** (732 mg, 2.69 mmol), Et_3N (0.749 mL, 5.37 mmol), TBSOTf (0.945 mL, 4.03 mmol) in CH_2Cl_2 (5.4 mL) and hexane/EtOAc (99.5:0.5 to 94:6) as an eluent. White solid (959 mg, 92%). Mp = 47.2–50.4 $^\circ\text{C}$. IR (neat) 829, 992, 1274, 1633, 1725, 2931, 2948, 3277 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.19 (s, 3H), 0.24 (s, 3H), 0.91 (s, 9H), 1.38–1.51 (m, 1H), 1.59–1.68 (m, 3H), 1.95 (t, $J = 2.7$ Hz, 1H), 2.15–2.21 (m, 2H), 3.09 (s, 2H), 3.67 (s, 3H), 4.05 (d, $J = 2.4$ Hz, 1H), 4.17 (d, $J = 2.4$ Hz, 1H), 7.07–7.12 (m, 2H), 7.17–7.25 (m, 3H). ^{13}C NMR (CDCl_3) δ -5.56, -4.97, 17.79, 18.53, 23.48, 25.33, 30.09, 37.03, 51.59, 56.82, 68.57, 83.93, 89.80, 126.50, 127.86, 130.21, 137.05, 158.19, 174.15. HRMS (ESI $^+$) Calcd for $\text{C}_{23}\text{H}_{34}\text{O}_3\text{Si}$ [M] $^+$: m/z 409.21694. Found: m/z 409.21632.

Scheme 9. Preparation of 1n.



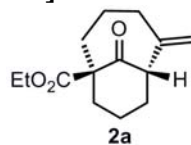
Methyl 2-[1-(*tert*-Butyldimethylsiloxy)vinyl]-2-(4-pentyn-1-yl)-6-heptynoate (1n)



The compound **3n** was prepared according to the procedure for the preparation of **3a**, employing methyl 2-acetyl-6-heptanoate (**20**) (929 mg, 5.10 mmol), NaH (245 mg, 6.13 mmol), 5-iodo-1-hexyne (1.52 g, 7.65 mmol) at room temperature overnight. Purification by silica gel chromatography (hexanes/EtOAc 98:2 to 75:25) afforded **3n** as a mixture of a small amount of a *O*-alkylation by-product (colorless oil, 917 mg, ca 73%). ¹H NMR (CDCl₃) δ 1.22–1.46 (m, 4H), 1.97–2.04 (m, 6H), 2.15 (s, 3H), 2.17–2.25 (m, 4H), 3.75 (s, 3H). Then silyl enolization of **3n** took place by using the procedure for the preparation **3a**, employing **3n** (917 mg, 3.69 mmol), Et₃N (0.772 mL, 5.54 mmol), TBSOTf (1.04 mL, 4.43 mmol) in CH₂Cl₂ (7.4 mL) and hexane/EtOAc (99.5/0.5 to 97/3) as the eluent. Colorless oil (887 mg, 48% from **19**). IR (neat) 626, 827, 1020, 1172, 1254, 1625, 1735, 2932, 2951, 3309 cm⁻¹; ¹H NMR (CDCl₃) δ 0.17 (s, 6H), 0.88 (s, 9H), 1.20–1.40 (m, 2H), 1.40–1.53 (m, 2H), 1.80–1.87 (m, 4H), 3.66 (s, 3H), 4.19 (q, *J* = 2.1 Hz, 2H). ¹³C NMR (CDCl₃) δ -5.27, 17.74, 18.60, 23.04, 25.30, 30.58, 51.70, 55.40, 68.52, 83.99, 89.12, 158.62, 174.63. Anal. Calcd for C₂₁H₃₄O₃Si: C, 69.56; H, 9.45%. Found: C, 69.56; H, 9.59%.

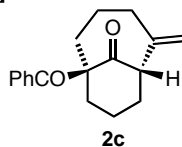
Cyclization Products.

Ethyl *cis*-5-Methylene-10-oxobicyclo[4.3.1]decane-1-carboxylate (**2a**)



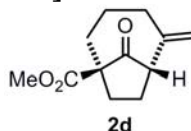
Colorless oil. IR (neat) 1175, 1232, 1704, 1732, 2935 cm⁻¹; ¹H NMR (CDCl₃) δ 1.28 (t, *J* = 7.2 Hz, 3H), 1.61–2.26 (m, 10H), 2.36–2.49 (m, 2H), 3.34 (br s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.93 (s, 1H), 5.03 (s, 1H). ¹³C NMR (CDCl₃) δ 13.78, 17.89, 23.66, 31.76, 34.00, 35.08, 35.26, 55.08, 60.85, 60.94, 112.50, 145.33, 173.58, 211.03. Anal. Calcd for C₁₄H₂₀O₃: C, 71.16; H, 8.53%. Found: C, 70.85; H, 86.68%.

cis-1-benzoyl-5-methylenebicyclo[4.3.1]decan-10-one (**2c**)



Colorless oil. IR (neat) 1230, 1446, 1677, 1697, 2932 cm⁻¹; ¹H NMR (CDCl₃) δ 1.72–1.83 (m, 1 H), 1.84–1.96 (m, 3H), 2.05–2.20 (m, 4H), 2.23–2.40 (m, 2 H), 2.40–2.55 (m, 2 H), 3.61 (br s, 1H), 4.96 (s, 1H), 5.10 (s, 1H), 7.36–7.49 (m, 2H), 7.45–7.52 (m, 1H), 7.66–7.71 (m, 2H). ¹³C NMR (CDCl₃) δ 18.79, 24.67, 32.46, 35.24, 36.33, 37.63, 54.61, 63.53, 113.17, 128.23, 129.50, 131.96, 135.10, 146.04, 201.06, 213.17. HRMS (ESI⁺) Calcd for C₁₈H₂₀O₂ [M+Na]⁺: *m/z* 291.13555. Found: *m/z* 291.13523.

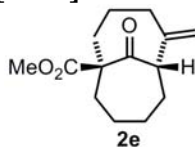
Methyl *cis*-5-Methylene-9-oxobicyclo[4.2.1]nonane-1-carboxylate (**2d**)



Colorless oil. IR (neat) 1174, 1208, 1268, 1243, 1727, 1749, 2935, 2949 cm⁻¹; ¹H NMR (CDCl₃) δ

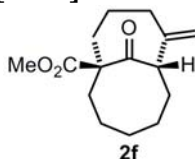
1.69–1.99 (m, 4H), 2.02–2.20 (m, 3H), 2.35–2.61 (m, 3H), 3.34 (dd, $J = 8.7, 2.1$ Hz, 1H), 3.74 (s, 3H), 4.81 (s, 1H), 4.89 (s, 1H). ^{13}C NMR (CDCl_3) δ 23.78, 28.19, 29.31, 34.31, 34.89, 52.45, 54.48, 60.14, 111.38, 146.20, 173.05, 214.61. HRMS (EI^+) Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3$ $[\text{M}]^+$: m/z 208.10994. Found: m/z 208.10967.

Methyl *cis*-5-Methylene-11-oxobicyclo[4.4.1]undecane-1-carboxylate (2e)



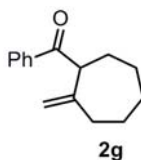
Colorless oil. IR (neat) 901, 1210, 1690, 1728, 2925, 2950 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.45–1.55 (m, 1H), 1.68–2.20 (m, 12H), 2.45–2.55 (m, 1H), 3.46–3.58 (m, 1H), 3.73 (s, 3H), 4.91 (s, 1H), 4.93 (s, 1H), 5.00 (s, 1H). ^{13}C NMR (CDCl_3) δ 24.71, 25.55, 25.69, 27.91, 30.73, 33.20, 36.23, 52.01, 61.79, 64.39, 113.20, 144.54. HRMS (EI^+) Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_3$ $[\text{M}]^+$: m/z 236.14124. Found: m/z 236.14115.

Methyl *cis*-8-Methylene-12-oxobicyclo[5.4.1]dodecane-1-carboxylate (2f)



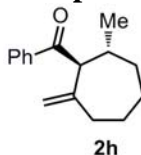
Colorless oil. IR (neat) 1220, 1241, 1438, 1683, 1731, 2929 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.17–1.34 (m, 1H), 1.40–1.56 (m, 1H), 1.56–1.99 (m, 9H), 2.03–2.14 (m, 1H), 2.03–2.14 (m, 1H), 2.30–2.56 (m, 4H), 3.34 (dd, $J = 9.0, 4.2$, 1H), 3.71 (s, 3H), 4.94 (s, 1H), 4.97 (s, 1H). ^{13}C NMR (CDCl_3) δ 23.06, 23.82, 24.77, 25.11, 30.08, 34.44, 34.68, 35.82, 51.88, 62.75, 63.35, 112.99, 145.77, 173.83, 213.61. HRMS (EI^+) Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_3$ $[\text{M}]^+$: m/z 250.15689. Found: m/z 250.15707.

2-Benzoyl-1-methylenecycloheptane (2g)



Colorless oil. IR (neat) 689, 1206, 1446, 1677, 2853, 2924 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.31–1.57 (m, 3H), 1.71–1.95 (m, 4H), 1.96–2.07 (m, 1H), 2.31–2.52 (m, 2H), 4.15 (dd, $J = 10.8, 4.8$, 1H), 4.72 (s, 1H), 4.89 (s, 1H), 7.40–7.47 (m, 2H), 7.50–7.57 (m, 1H), 7.91–7.97 (m, 2H). ^{13}C NMR (CDCl_3) δ 27.43, 28.53, 29.46, 30.69, 35.24, 52.54, 114.69, 128.53 (2C), 132.72, 136.83, 149.57, 201.40. HRMS (EI^+) Calcd for $\text{C}_{15}\text{H}_{18}\text{O}$ $[\text{M}]^+$: m/z 214.13576. Found: m/z 214.13583.

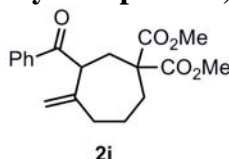
***trans*-1-Benzoyl-7-methyl-2-methylenecycloheptane (2h)**



Colorless oil. IR (neat) 697, 1206, 1446, 1675, 2853, 2922 cm^{-1} ; ^1H NMR (CDCl_3) δ 0.91 (d, $J = 6.6$ Hz, 3H), 1.34–1.69 (m, 4H), 1.71–1.89 (m, 2H), 2.18–2.27 (m, 1H), 2.30–2.40 (m, 1H), 2.41–2.52 (m, 1H), 3.94 (d, $J = 9.9$ Hz, 1H), 4.78 (s, 1H), 4.87 (s, 1H), 7.42–7.49 (m, 2H), 7.51–7.58 (m, 1H), 7.94–8.00 (m, 2H). ^{13}C NMR (CDCl_3) δ 22.37, 27.96, 31.52, 34.47, 34.98, 35.30, 60.71, 115.43, 128.54, 128.60, 132.72, 137.52, 148.42, 201.03. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$: C, 84.16; H, 8.83%. Found: C, 83.94; H, 8.93%. HRMS (EI^+) Calcd for $\text{C}_{16}\text{H}_{20}\text{O}$ $[\text{M}]^+$: m/z 228.15142. Found: m/z 228.15135. The

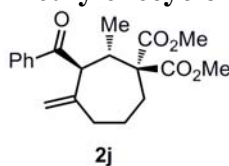
relative configuration of Bz and Me group was determined by comparing the coupling constant between H_a and H_b and that in the compound **2k**.

Dimethyl *trans*-3-Benzoyl-4-methylenecycloheptane-1,1-dicarboxylate (2i**)**



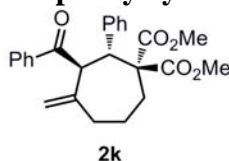
Colorless oil. IR (neat) 690, 1207, 1225, 1239, 1681, 1728, 2952 cm⁻¹; ¹H NMR (CDCl₃) δ 1.52–1.70 (m, 1H), 1.87–2.03 (m, 2H), 2.11 (dd, *J* = 14.4 Hz, 11.4 Hz, 1H), 2.30–2.47 (m, 2H), 2.47–2.58 (m, 1H), 2.73 (ddd, *J* = 14.4, 3.0, 1.5 Hz, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 4.39 (dd, *J* = 11.4, 3.0 Hz, 1H), 4.72 (s, 1H), 4.87 (s, 1H), 7.40–7.47 (m, 2H), 7.51–7.58 (m, 1H), 7.89–7.94 (m, 2H). ¹³C NMR (CDCl₃) δ 22.67, 31.78, 34.75, 36.17, 47.93, 52.41, 52.69, 57.16, 115.34, 128.53, 128.56, 132.93, 136.33, 147.65, 172.04, 172.88, 199.81. HRMS (EI⁺) Calcd for C₁₉H₂₂O₅ [M]⁺: *m/z* 330.14672. Found: *m/z* 330.14679.

Dimethyl *trans*-3-Benzoyl-2-methyl-4-methylenecycloheptane-1,1-dicarboxylate (2j**)**

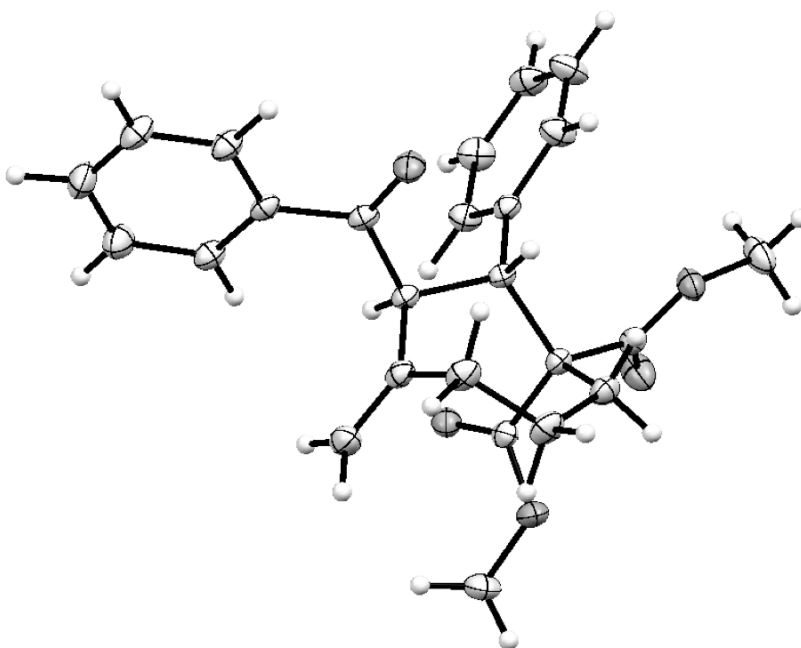


White solid (recrystallization from hot hexane gave a colorless crystalline). IR (neat) 699, 1245, 1672, 1724, 1743, 2939, 2956 cm⁻¹; Mp = 47.2–50.4 °C. ¹H NMR (CDCl₃) δ 1.04 (d, *J* = 6.6 Hz, 3H), 1.40–1.58 (m, 1H), 1.88–2.00 (m, 1H), 2.01–2.15 (m, 2H), 2.27 (td, *J* = 12.6, 3.0 Hz, 1H), 2.37 (dt, *J* = 14.4, 4.2 Hz, 1H), 3.04 (dq, *J* = 10.5, 6.6 Hz, 1H, –CH_a(Me)–), 3.73 (s, 3H), 3.76 (s, 3H), 4.69 (d, *J* = 10.5 Hz, 1H, –CH_b(Bz)–), 4.84 (s, 1H), 4.88 (s, 1H), 7.42–7.49 (m, 2H), 7.52–7.59 (m, 1H), 7.98–8.04 (m, 2H). ¹³C NMR (CDCl₃) δ 17.90, 28.69, 31.47, 37.00, 38.88, 51.78, 52.30, 59.05, 61.38, 118.46, 128.61, 128.84, 133.04, 136.90, 146.67, 171.04, 173.05, 199.60. Anal. Calcd for C₂₀H₂₄O₅: C, 69.75; H, 7.02%. Found: C, 69.76; H, 7.08%. The relative configuration of Bz and Me group was determined by comparing the coupling constant between H_a and H_b and that in the compound **2k**.

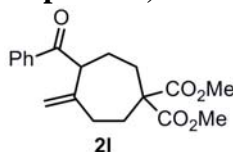
Dimethyl *trans*-3-Benzoyl-4-methylene-2-phenylcycloheptane-1,1-dicarboxylate (2k**)**



White solid. IR (neat) 700, 1246, 1672, 1725, 1744, 2939, 2955 cm⁻¹; Mp = 150.5–151.0 °C. ¹H NMR (CDCl₃) δ 1.47 (distorted qt, *J* = 13.2, 3.6 Hz, 1H), 2.01–2.11 (m, 1H), 2.16–2.25 (m, 1H), 2.32 (td, *J* = 13.8, 4.5 Hz, 1H), 2.43–2.57 (m, 2H), 3.13 (s, 3H), 3.76 (s, 3H), 4.12 (d, *J* = 11.4 Hz, 1H, –CH_a(Ph)–), 4.91 (s, 1H), 4.95 (s, 1H), 5.46 (d, *J* = 11.4 Hz, 1H, –CH_b(Bz)–), 7.02–7.08 (m, 1H), 7.11–7.18 (m, 2H), 7.28–7.35 (m, 2H), 7.39–7.45 (m, 1H), 7.60 (br s, 2H), 7.72–7.77 (m, 2H). ¹³C NMR (CDCl₃) δ 29.27, 31.73, 38.37, 51.83, 51.92, 52.06, 58.03, 63.09, 118.90, 127.09, 127.92, 128.32, 128.62, 130.51, 132.62, 132.64, 140.05, 146.69, 171.12, 171.72, 199.03. Anal. Calcd for C₂₅H₂₆O₅: C, 73.87; H, 6.45%. Found: C, 73.86; H, 6.47%. The relative configuration was determined by X-ray analysis as shown below. X-ray quality crystals were grown from hot hexane. Crystallographic data for the structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 787890). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Fax: 44-1223-3360033 or E-mail: deposit@ccdc.cam.ac.uk

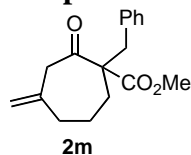


Dimethyl 5-Benzoyl-4-methylenecycloheptane-1,1-dicarboxylate (2l)



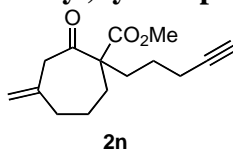
Colorless oil. IR (neat) 691, 1169, 1209, 1237, 1677, 1728, 2953 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.83–2.07 (m, 4H), 2.39–2.63 (m, 4H), 3.72 (s, 3H), 3.76 (s, 3H), 4.25 (dd, $J = 9.3, 5.7$ Hz, 1H), 4.77 (s, 1H), 4.96 (s, 1H), 7.42–7.50 (m, 2H), 7.52–7.59 (m, 2H), 7.90–7.96 (m, 2H). ^{13}C NMR (CDCl_3) δ 25.27, 31.12, 31.15, 34.92, 51.94, 52.49, 52.61, 57.79, 116.04, 128.59, 128.63, 132.99, 136.49, 147.85, 171.82, 173.04, 200.58. HRMS (EI^+) Calcd for $\text{C}_{19}\text{H}_{22}\text{O}_5$ $[\text{M}]^+$: m/z 330.14672. Found: m/z 330.14672.

Methyl 1-Benzyl-4-methylene-2-oxocycloheptanecarboxylate (2m)



Colorless oil. IR (neat) 691, 1169, 1209, 1237, 1677, 1728, 2953 cm^{-1} ; ^1H NMR (CDCl_3) δ 1.62–1.83 (m, 3H), 2.00–2.10 (m, 1H), 2.32–2.42 (m, 1H), 2.97 (d, $J = 13.5$ Hz, 1H), 3.10 (d, $J = 14.7$ Hz, 1H), 3.32 (d, $J = 13.5$ Hz, 1H), 3.44 ($J = 14.7$, 1H), 3.60 (s, 3H), 4.87 (s, 1H), 4.90 (s, 1H), 7.05–7.10 (m, 2H), 7.20–7.28 (m, 3H). ^{13}C NMR (CDCl_3) 25.06, 32.75, 36.52, 41.65, 51.52, 51.93, 63.84, 116.10, 126.86, 128.12, 130.41, 136.60, 141.78, 171.92, 206.21. Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{O}_3$: C, 74.94; H, 7.40%. Found: C, 74.88; H, 7.42%.

Methyl 4-Methylene-2-oxo-1-(4-pentyn-1-yl)cycloheptanecarboxylate (2n)



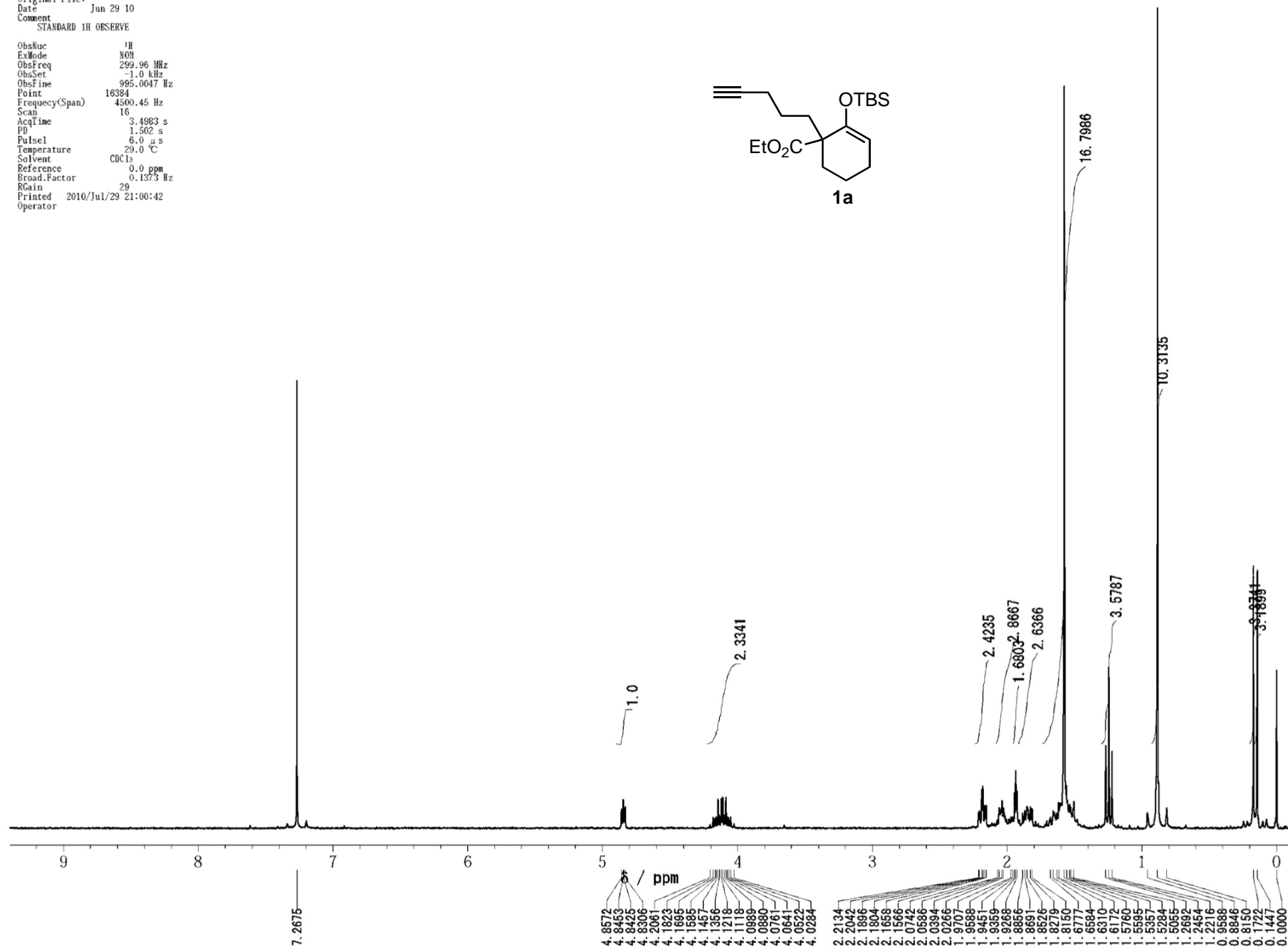
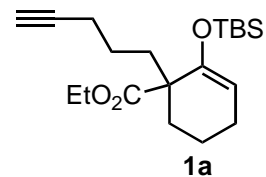
Colorless oil. IR (neat) 637, 1172, 1214, 1434, 1701, 1738, 2948, 3288 cm^{-1} ; ^1H NMR (CDCl_3) δ

1.34–1.54 (m, 2H), 1.58–1.93 (m, 4H), 1.95 (t, $J = 2.7$ Hz), 1.96–2.28 (m, 5H), 2.32–2.43 (m, 1H), 3.21 (d, $J = 15.0$ Hz, 1H), 3.46 (d, $J = 15.0$ Hz, 1H), 3.70 (d, $J = 15.0$ Hz, 1H), 3.70 (s, 3H), 4.89 (s, 1H), 4.94 (s, 1H). ^{13}C NMR (CDCl_3) 18.61, 23.56, 25.15, 33.50, 35.13, 36.59, 51.30, 52.12, 62.07, 68.59, 83.80, 116.22, 141.98, 172.53, 206.41. HRMS (EI^+) Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: m/z 248.14124. Found: m/z 248.14087.

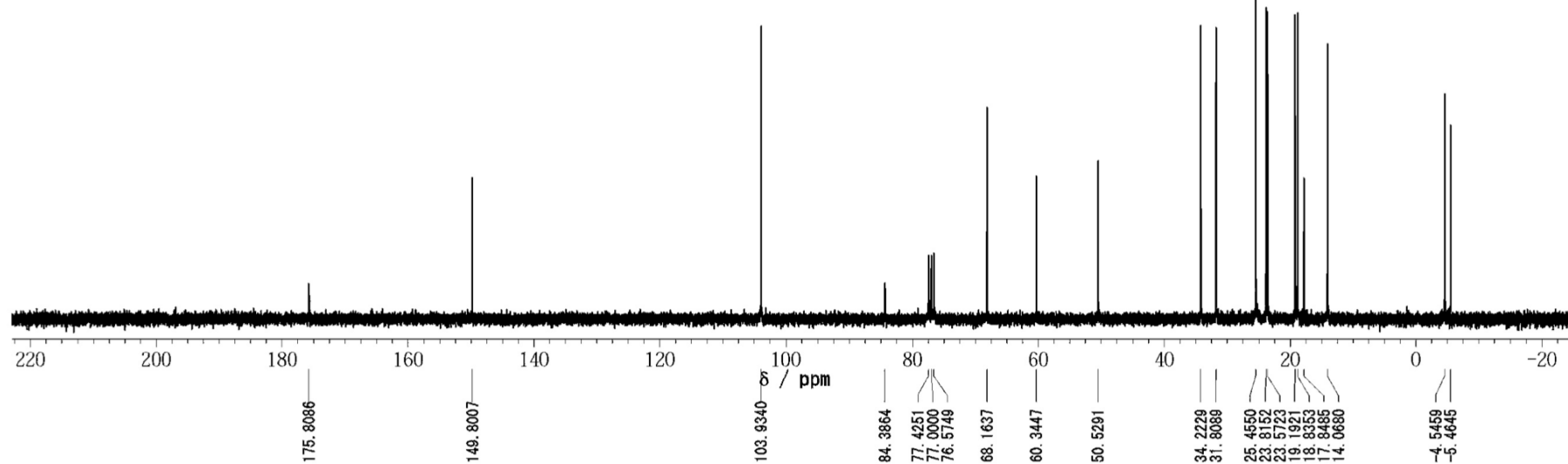
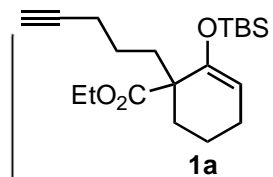
References

- 1) Ochida, A.; Ito, H.; Sawamura, M. *J. Am. Chem. Soc.* **2006**, *128*, 16486–16487.
- 2) Williams, D. B.; Stoll, M. E.; Scott, B. L.; Costa, D. A.; Oldham, W. J. Jr. *Chem. Commun.* **2005**, 1438–1440.
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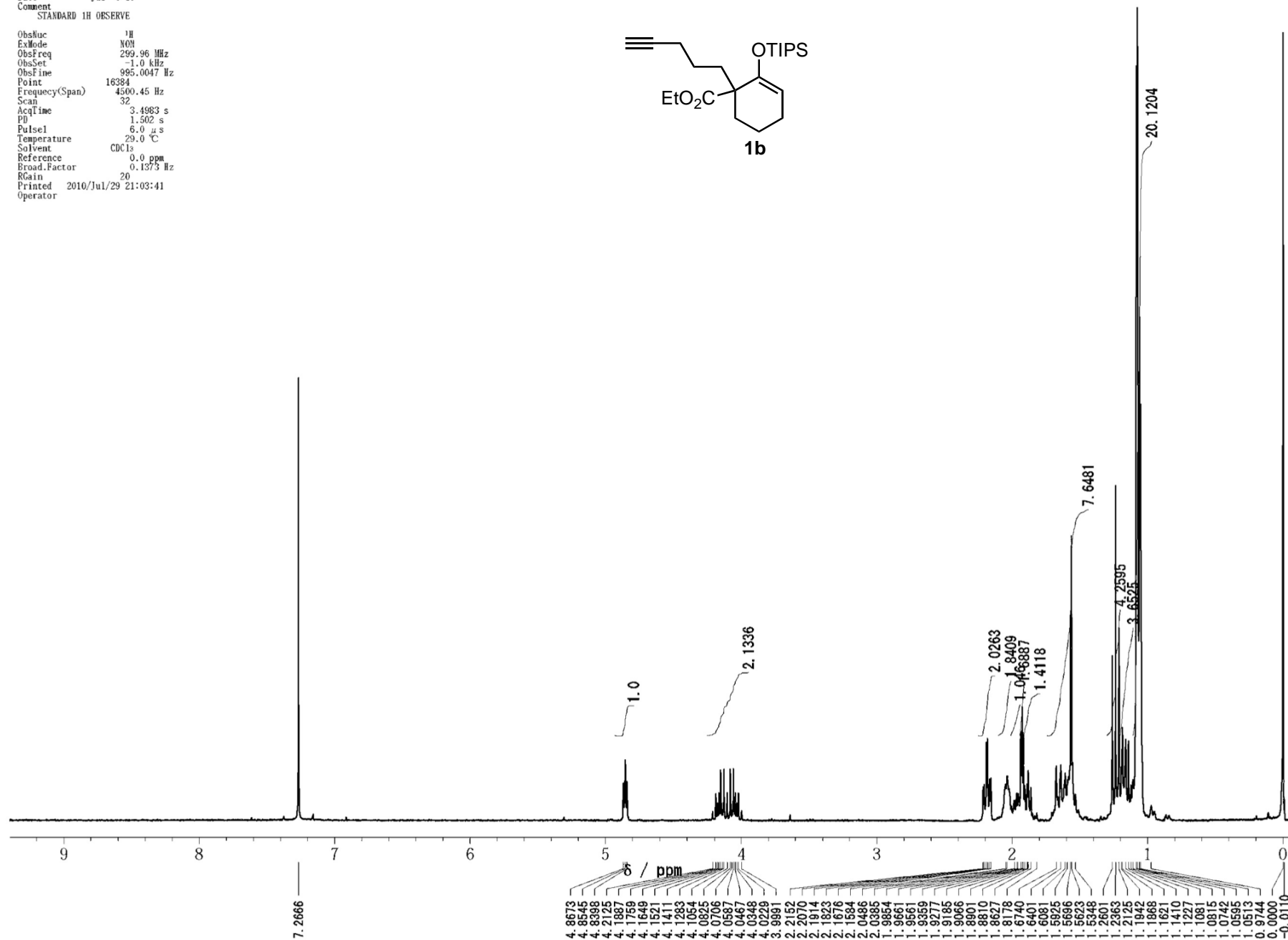
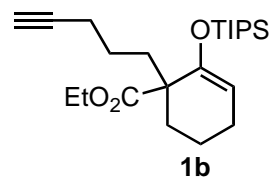
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 PD 1.502 s
 Pulse1 6.0 μ s
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 Broad.Factor 0.1373 Hz
 RGain 29
 Printed 2010/Jul/29 21:00:42
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 Date Jun 29 10
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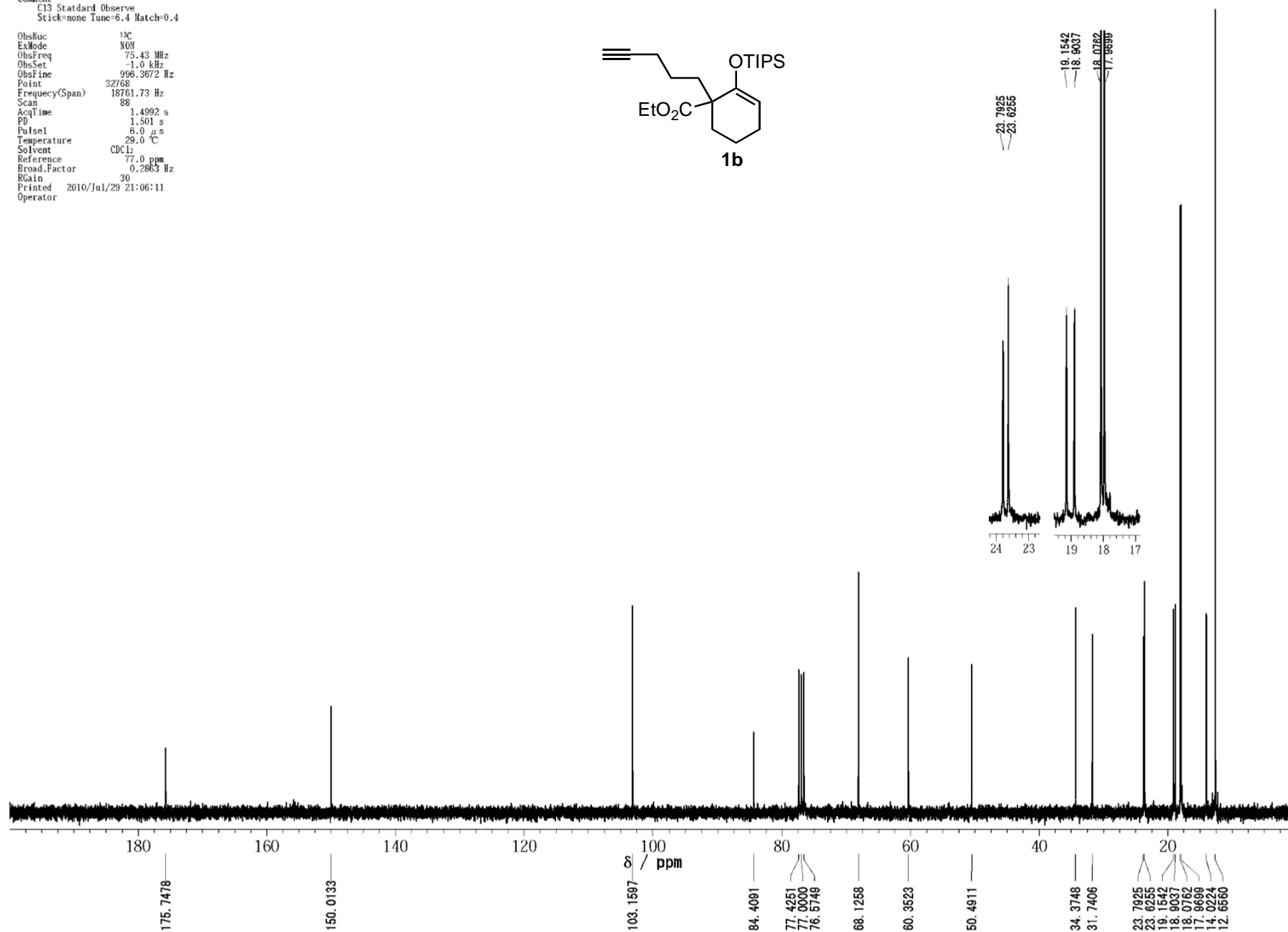
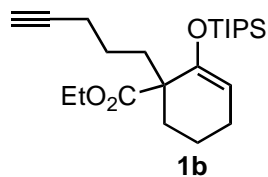


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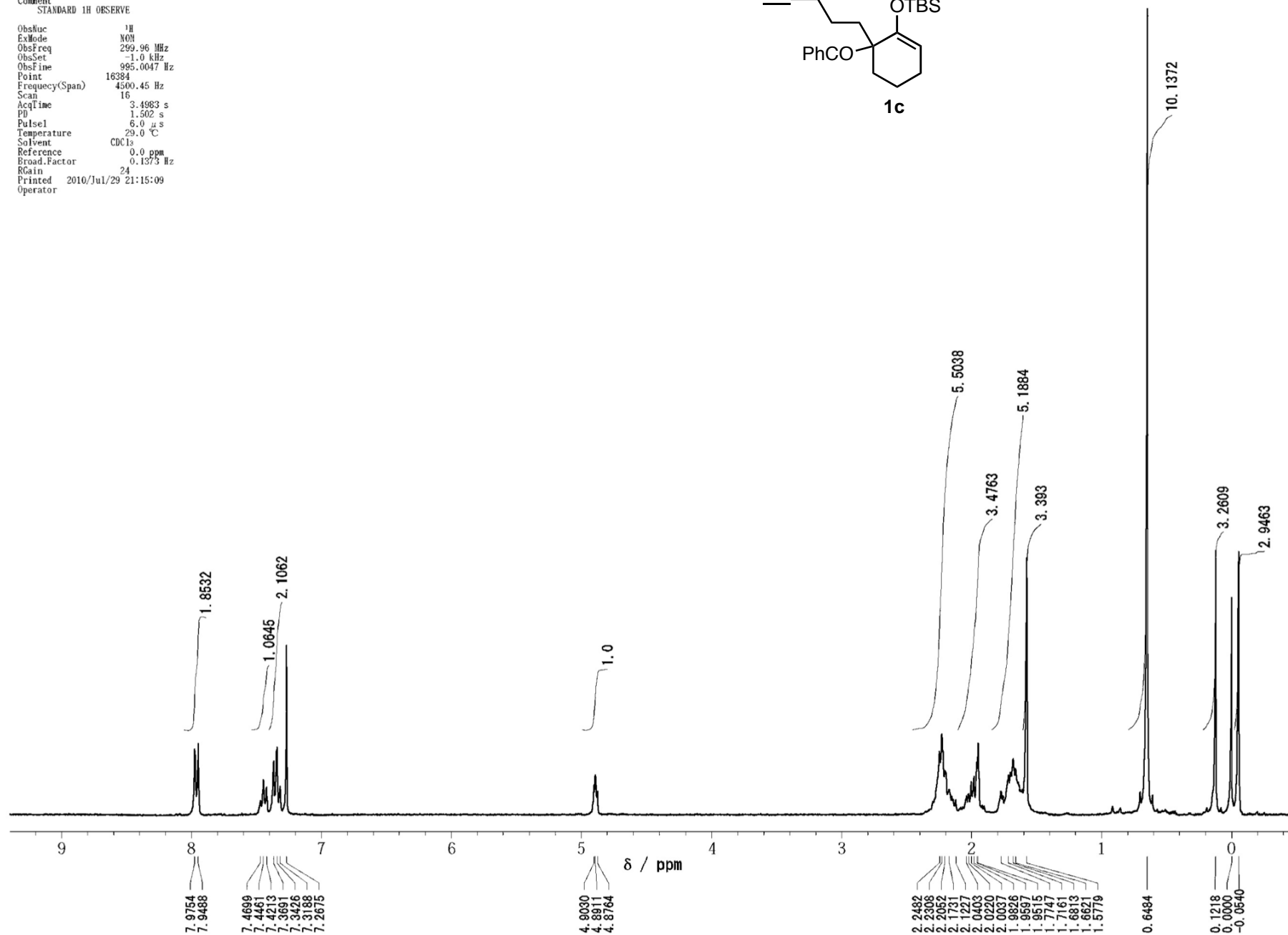
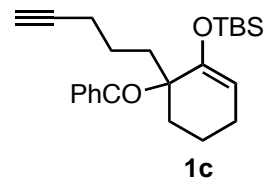


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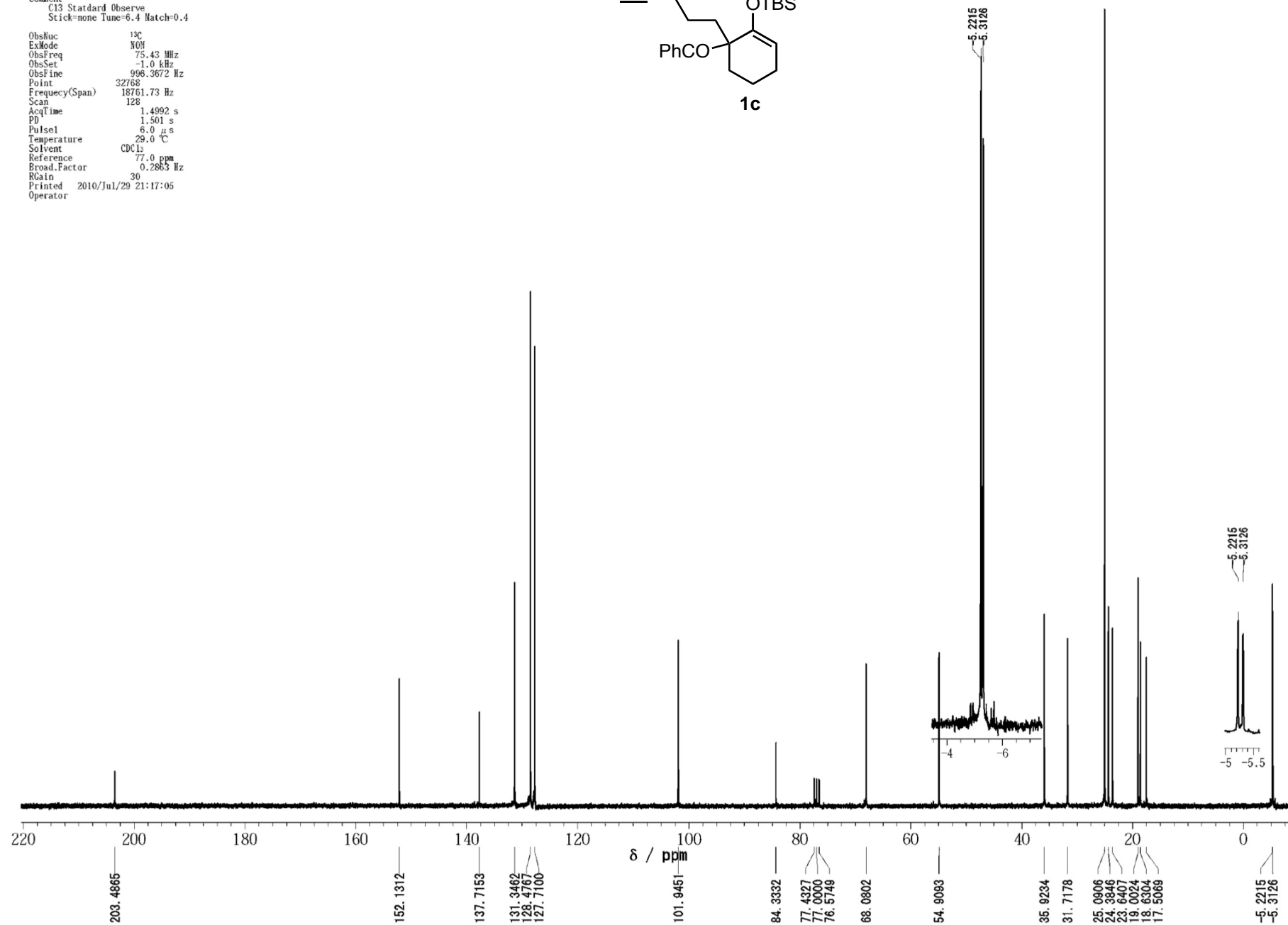
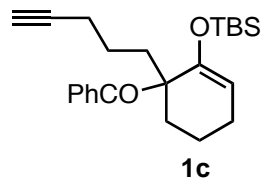


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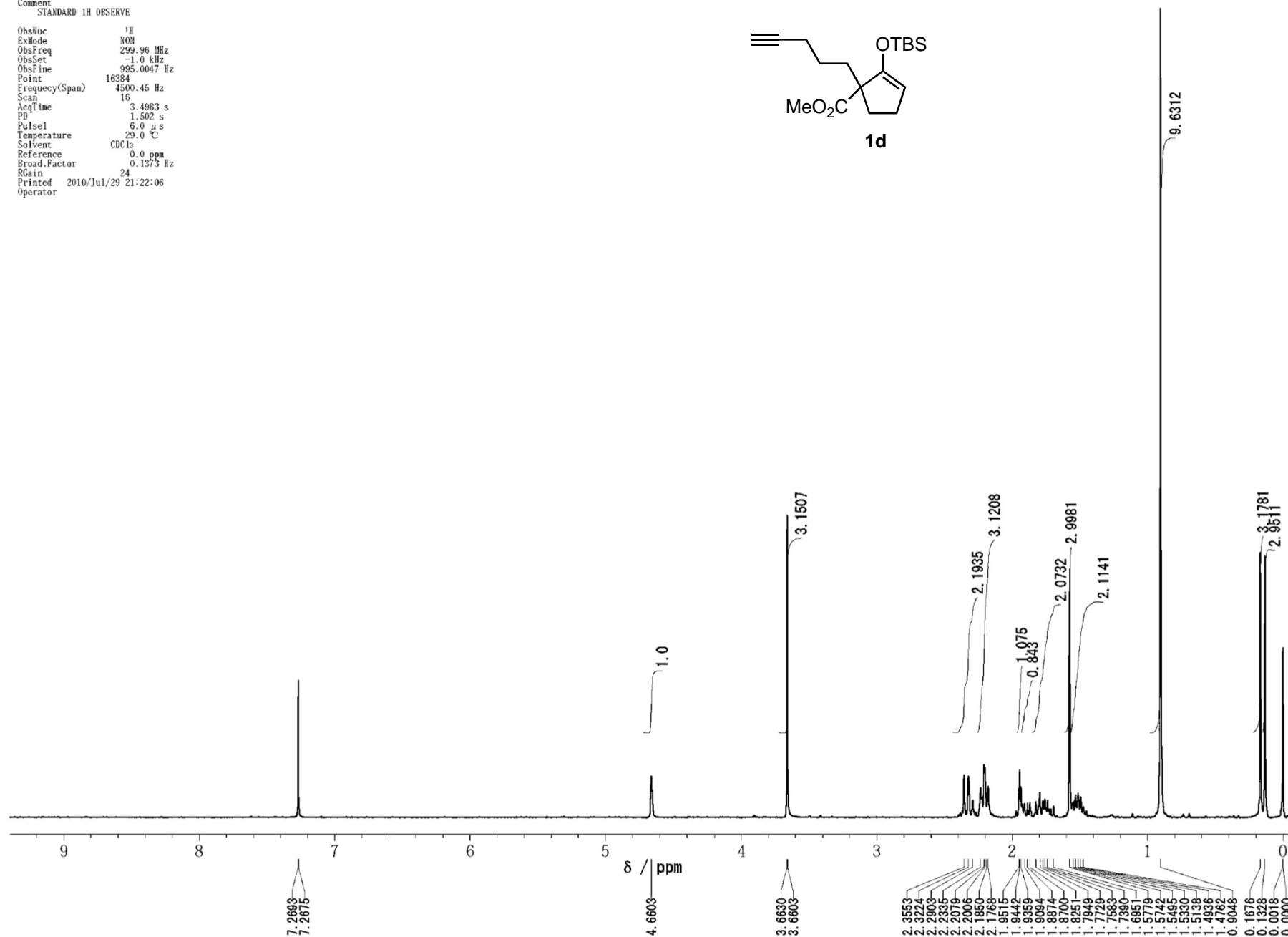
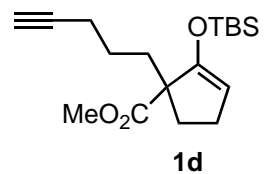


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 PD 1.501 s
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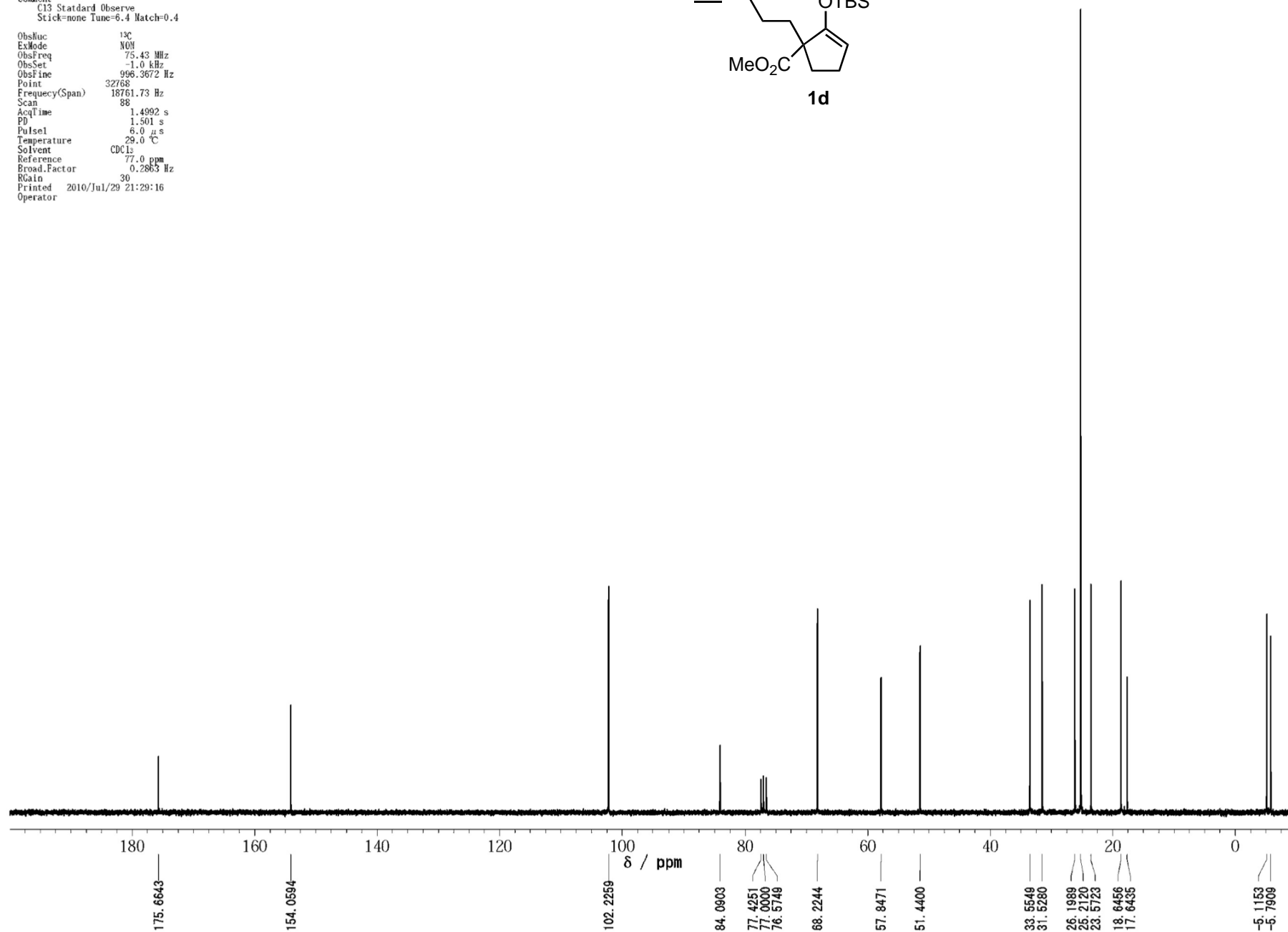
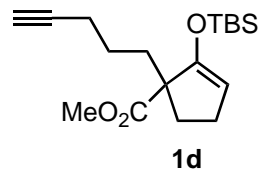


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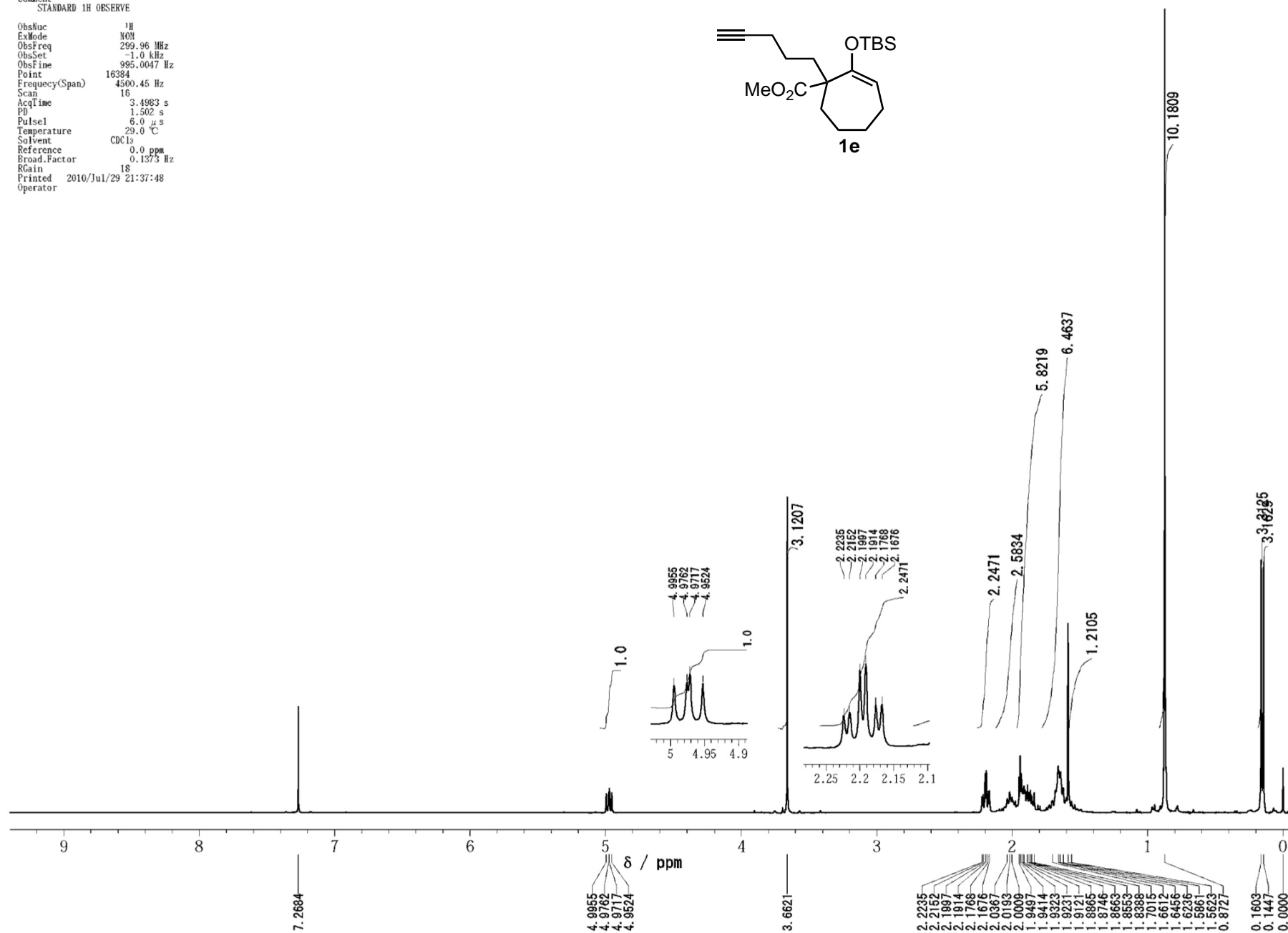
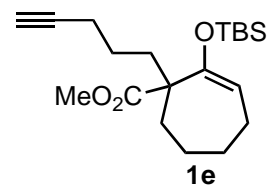
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 Pulse 6.0 μ s
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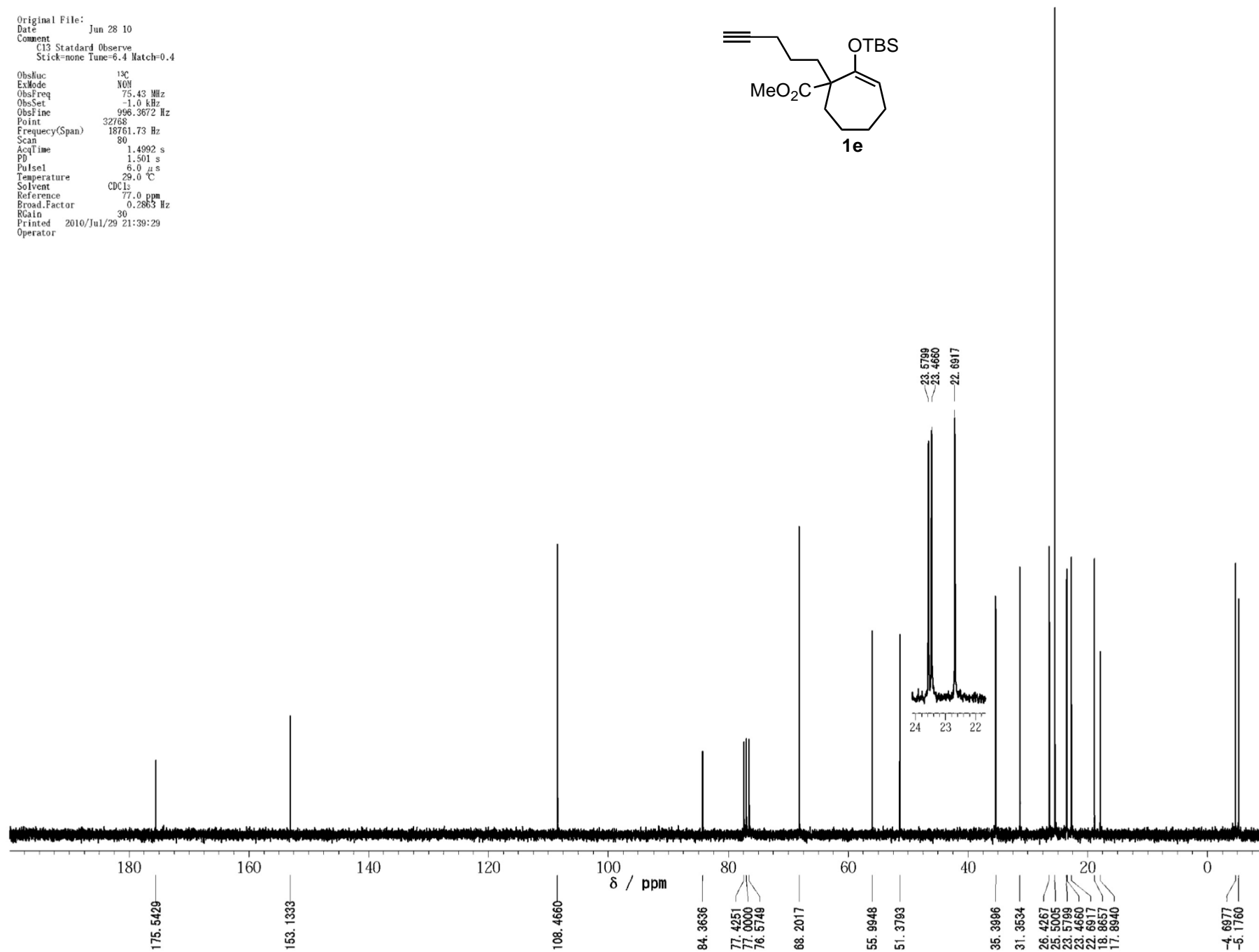
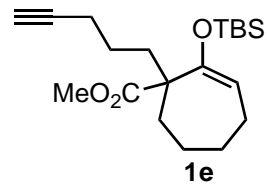
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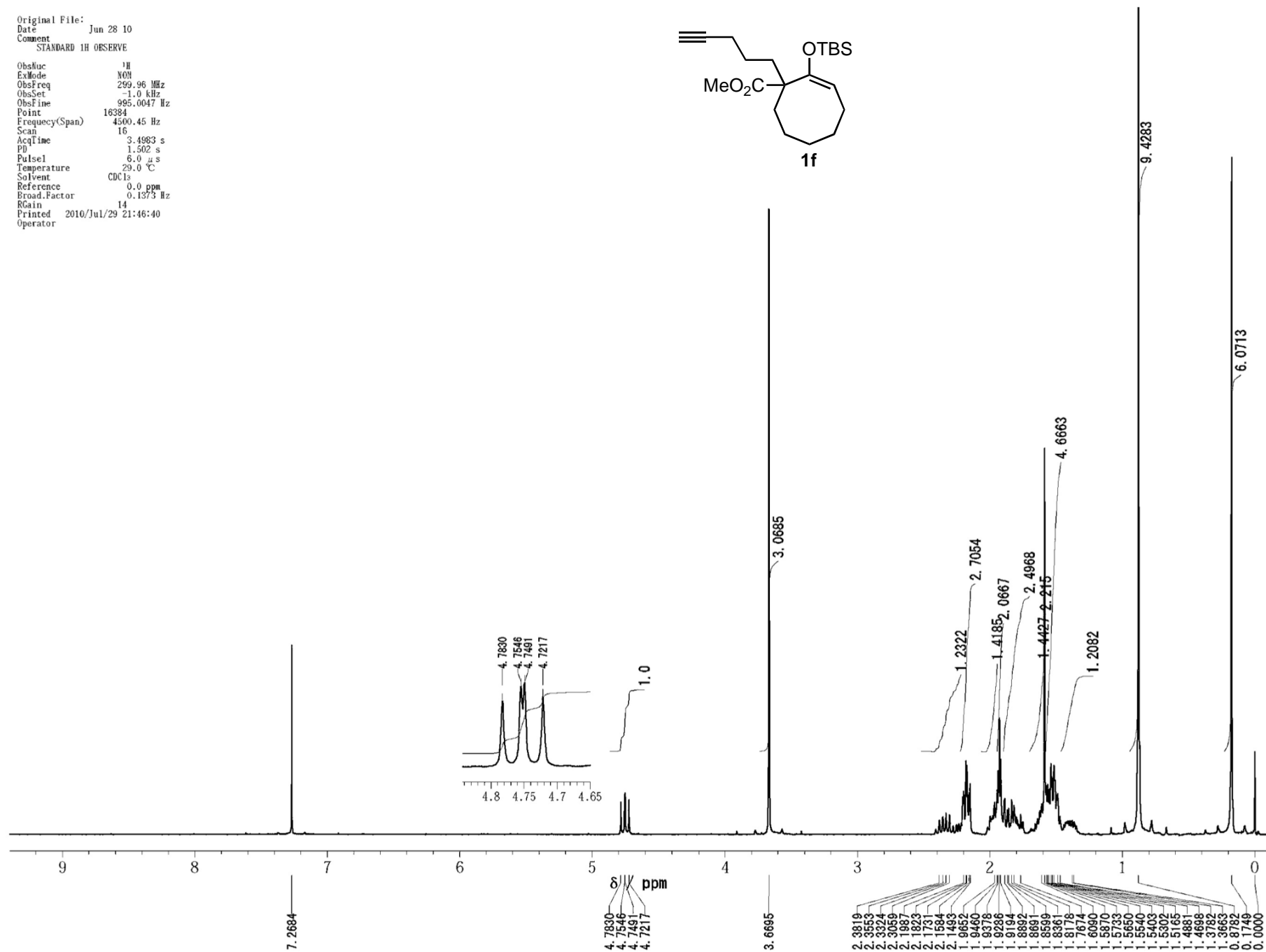
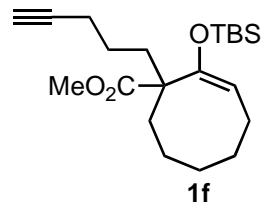


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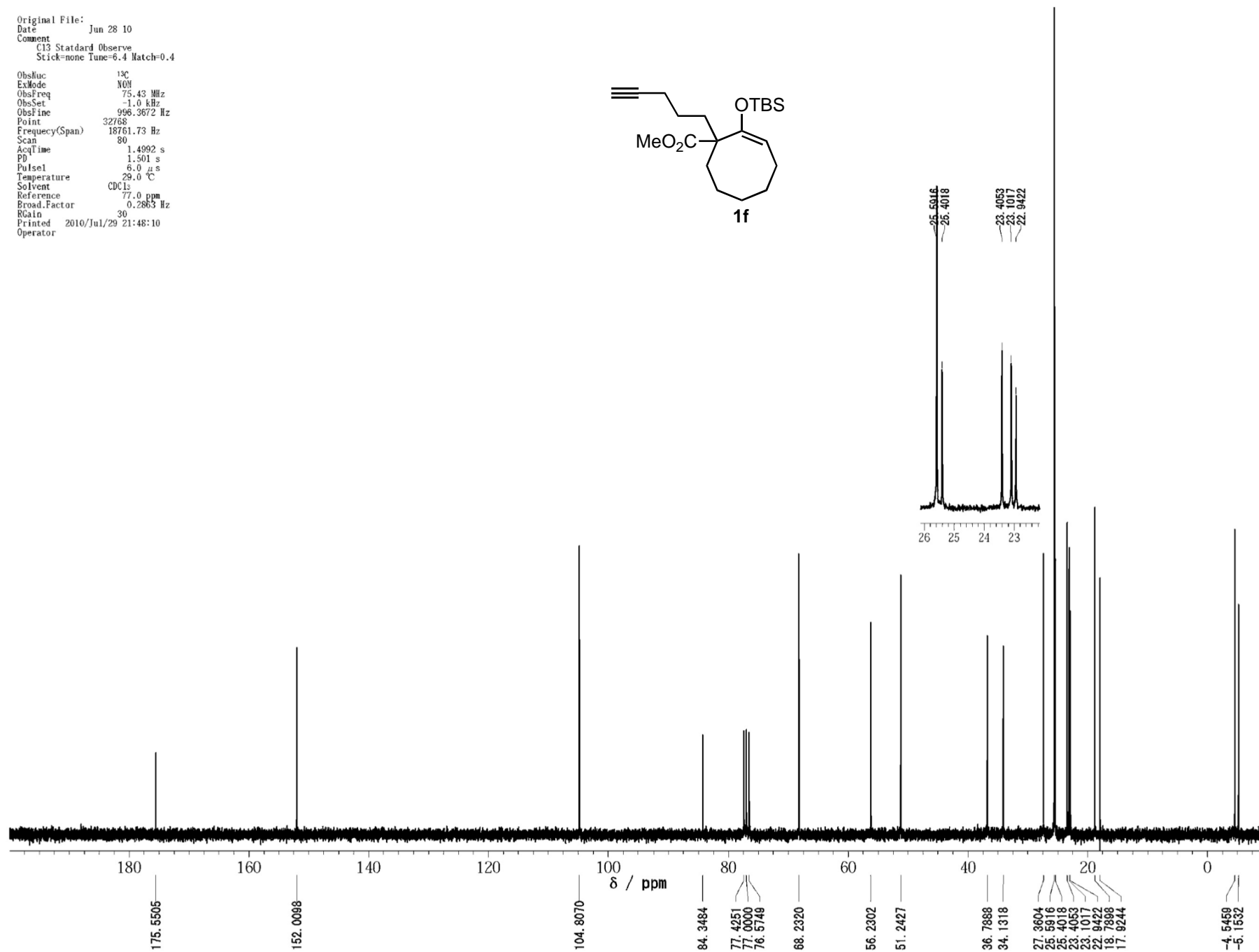
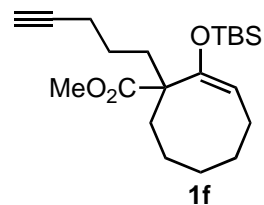


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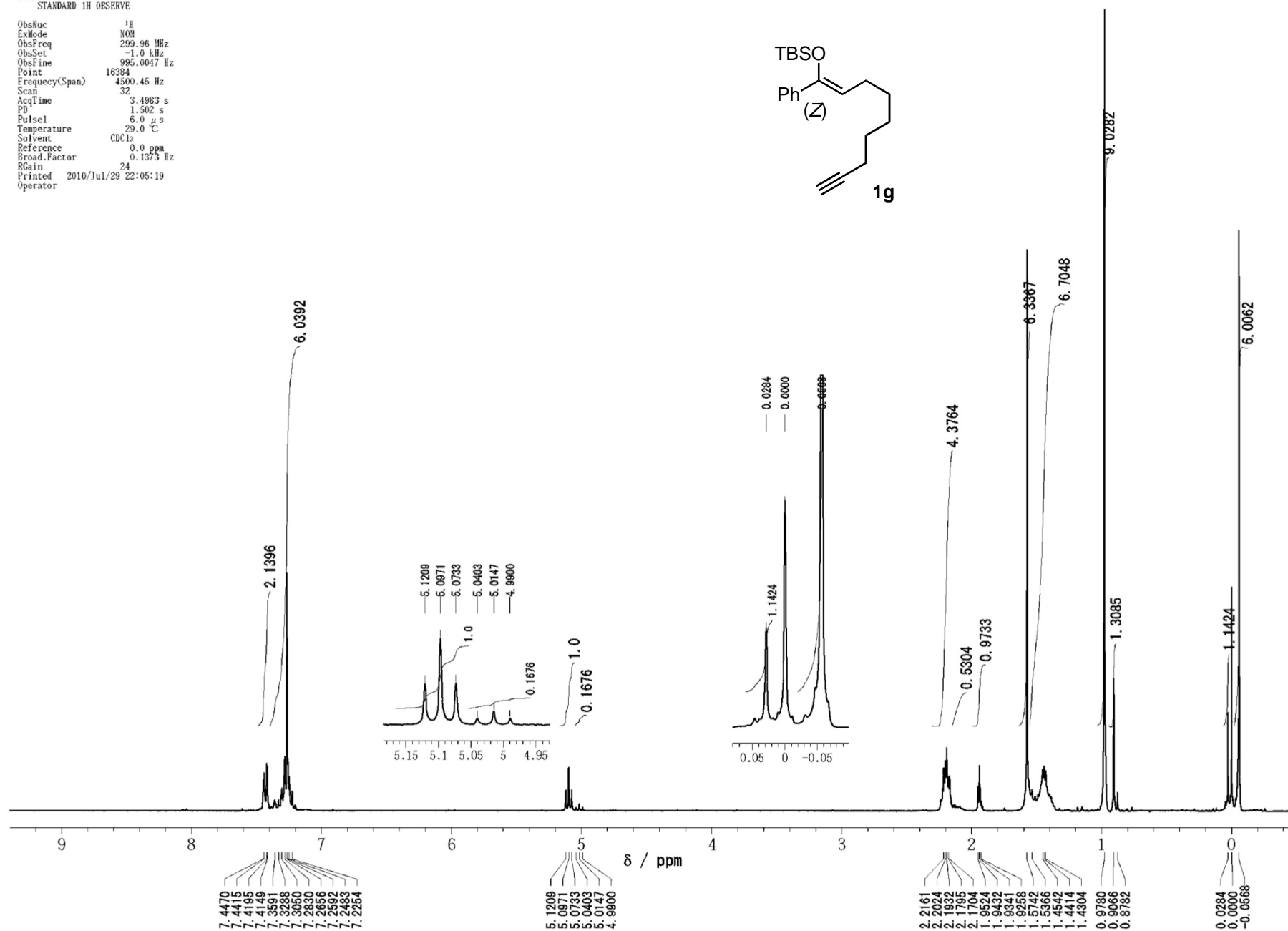
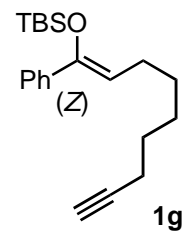


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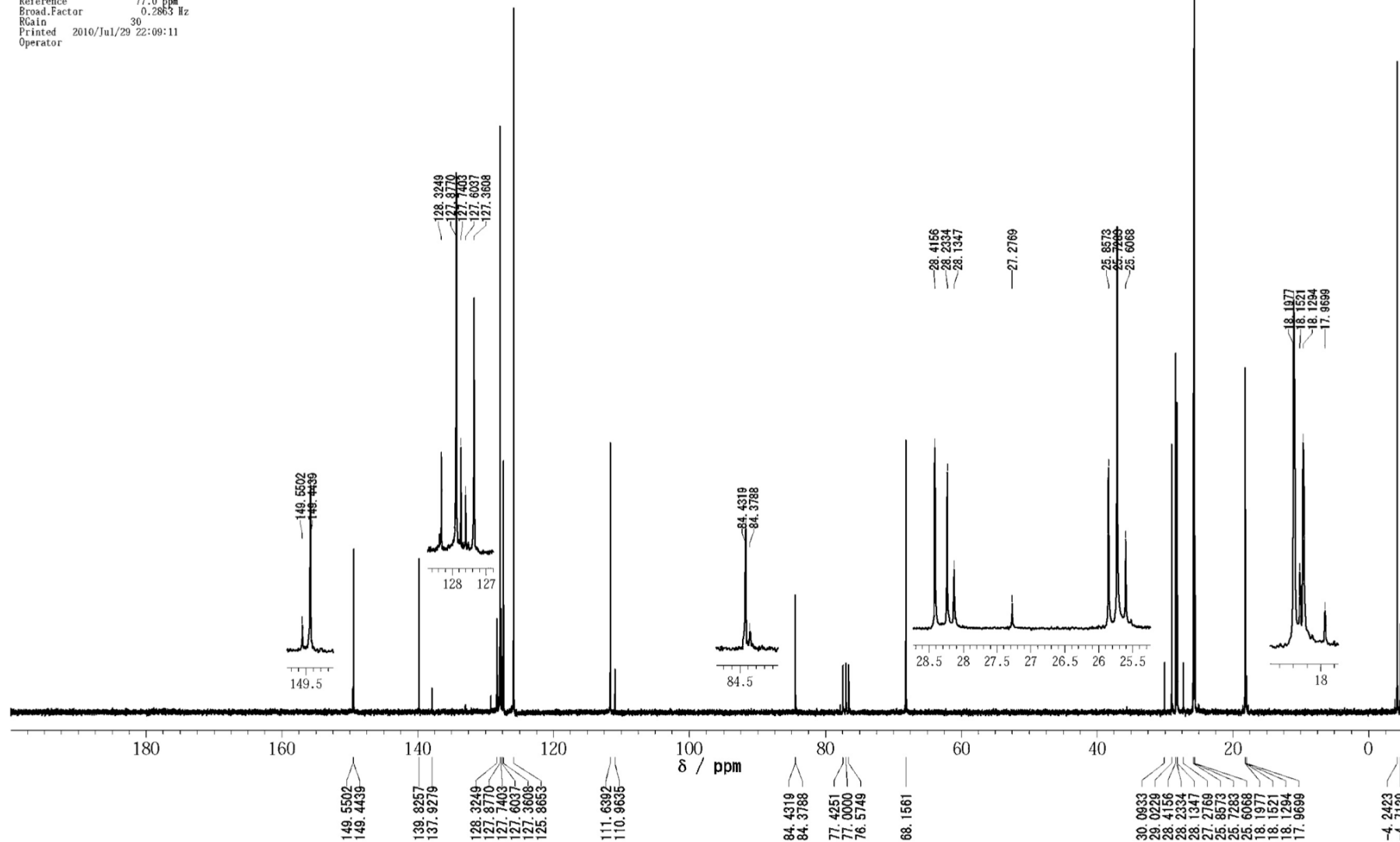
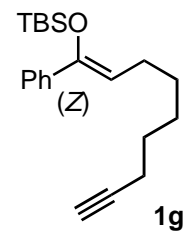


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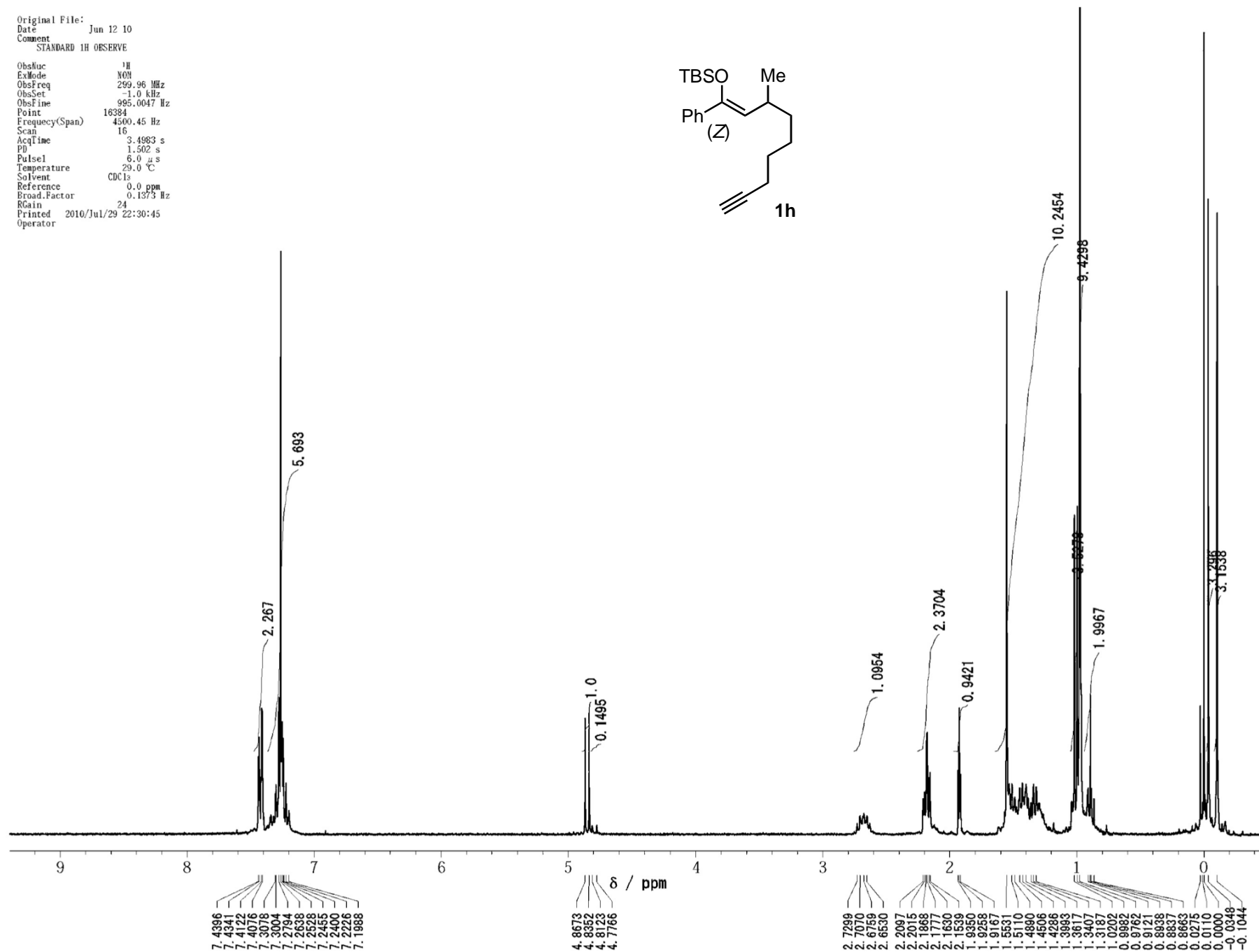
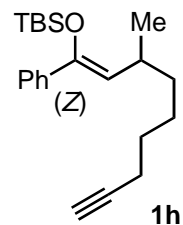


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ObsRuc 13C
 ExMode N0H
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 120
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 22:09:11
 Operator

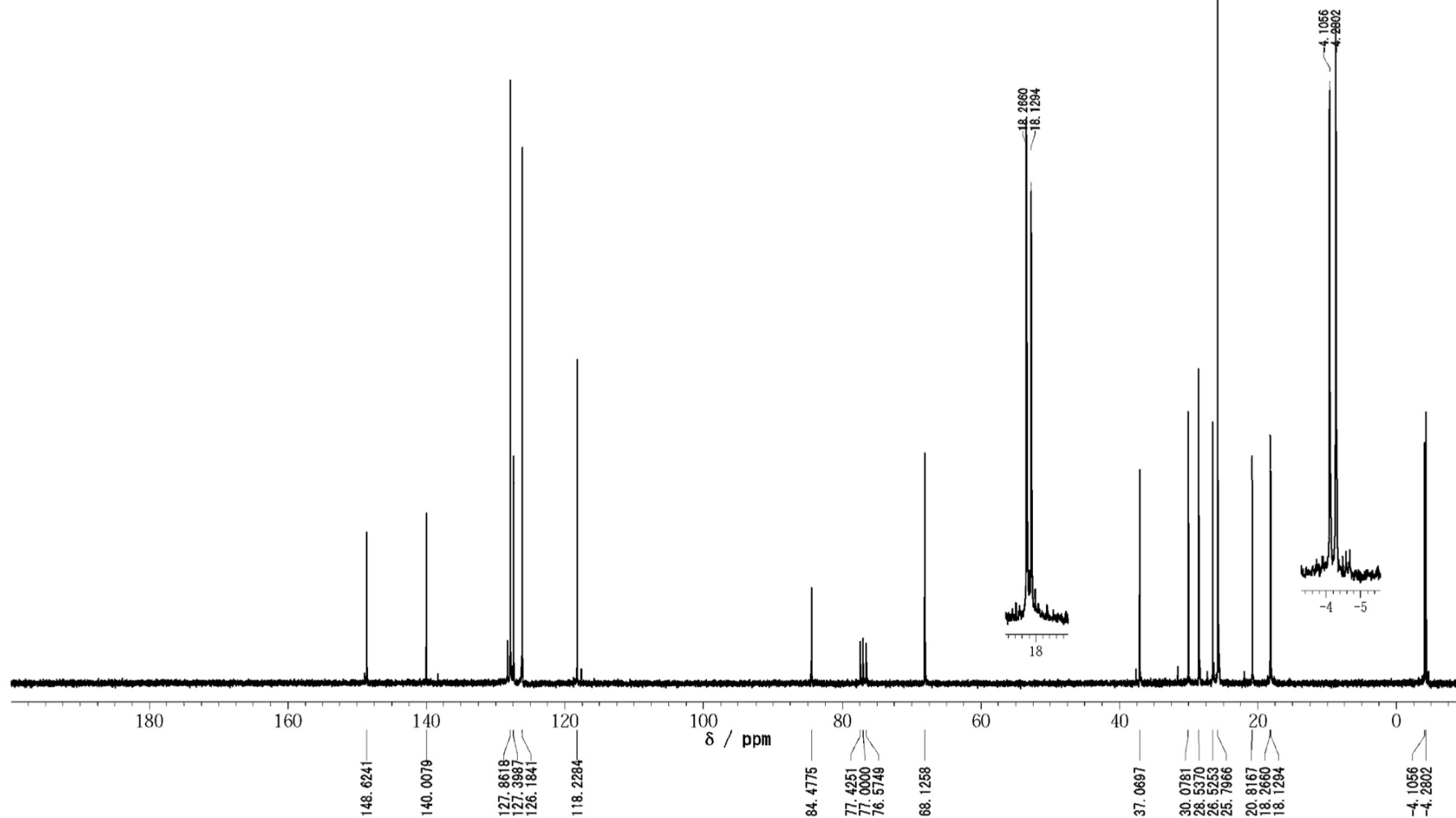
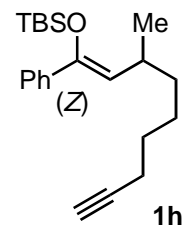


Original File:
 Date Jun 12 10
 Comment
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 ObsMod 1H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 16
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/29 22:30:45
 Operator



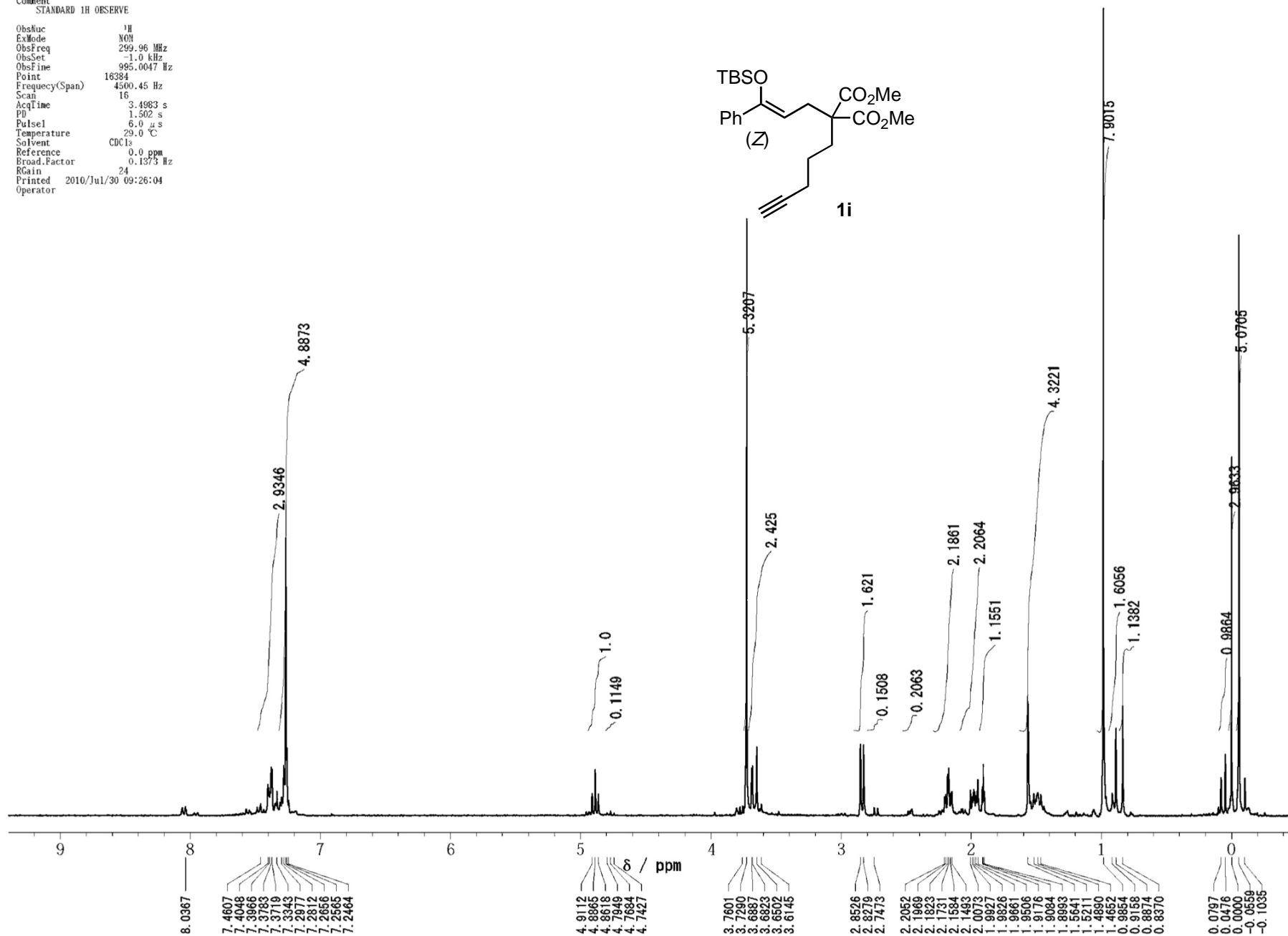
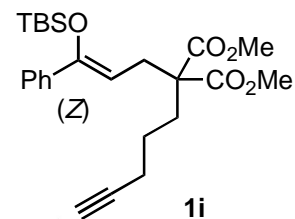
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Date Jun 12 10
Comment
C13 Standard Observe
Stick=none Tune=6.4 Match=0.4

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ExMode NOM
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequency(Span) 18761.73 Hz
Scan 128
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2010/Jul/29 22:32:04
Operator



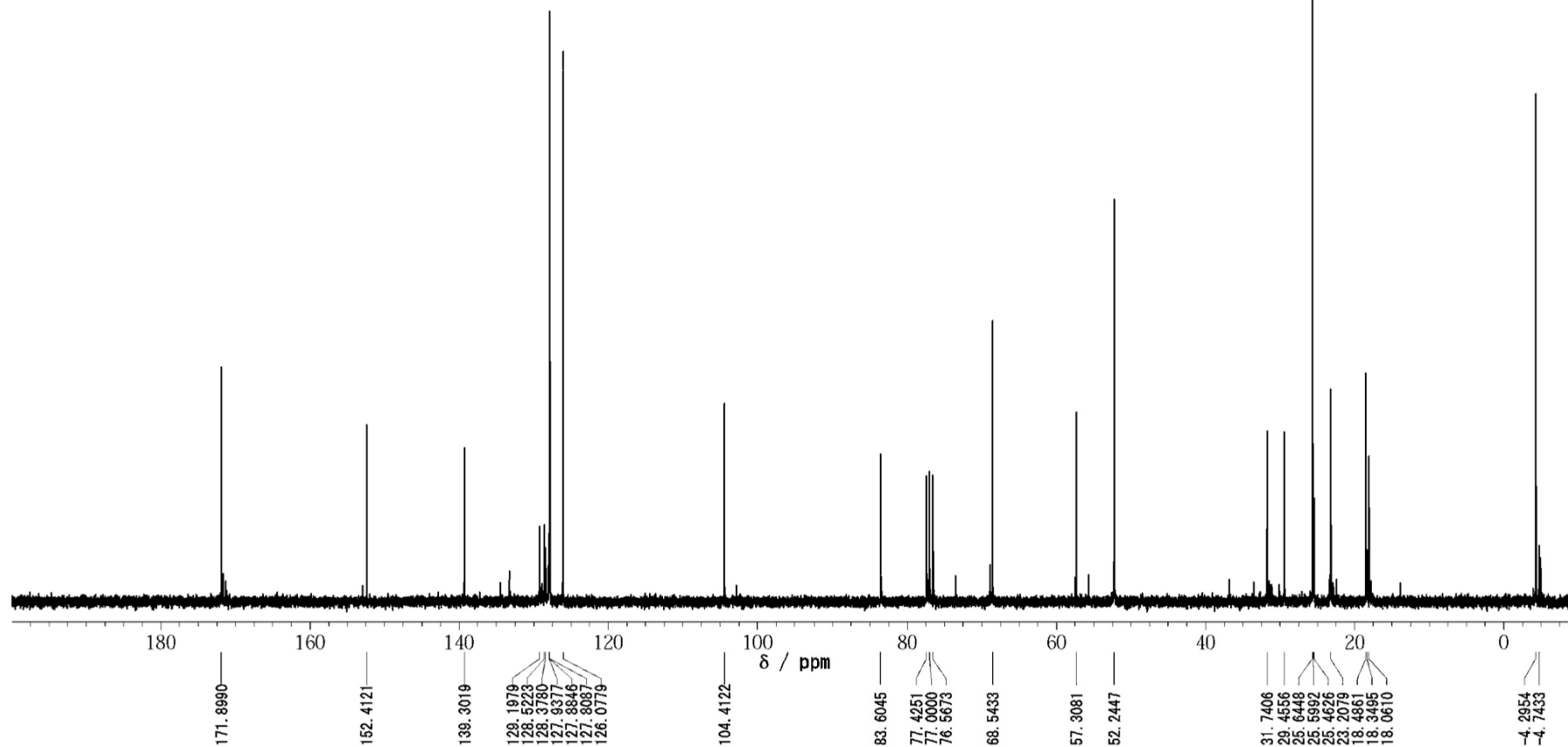
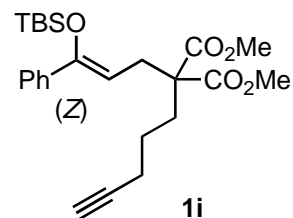
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Date 10/Jun/2012 00:00:00
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ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 24
Printed 2010/Jul/30 09:26:04
Operator

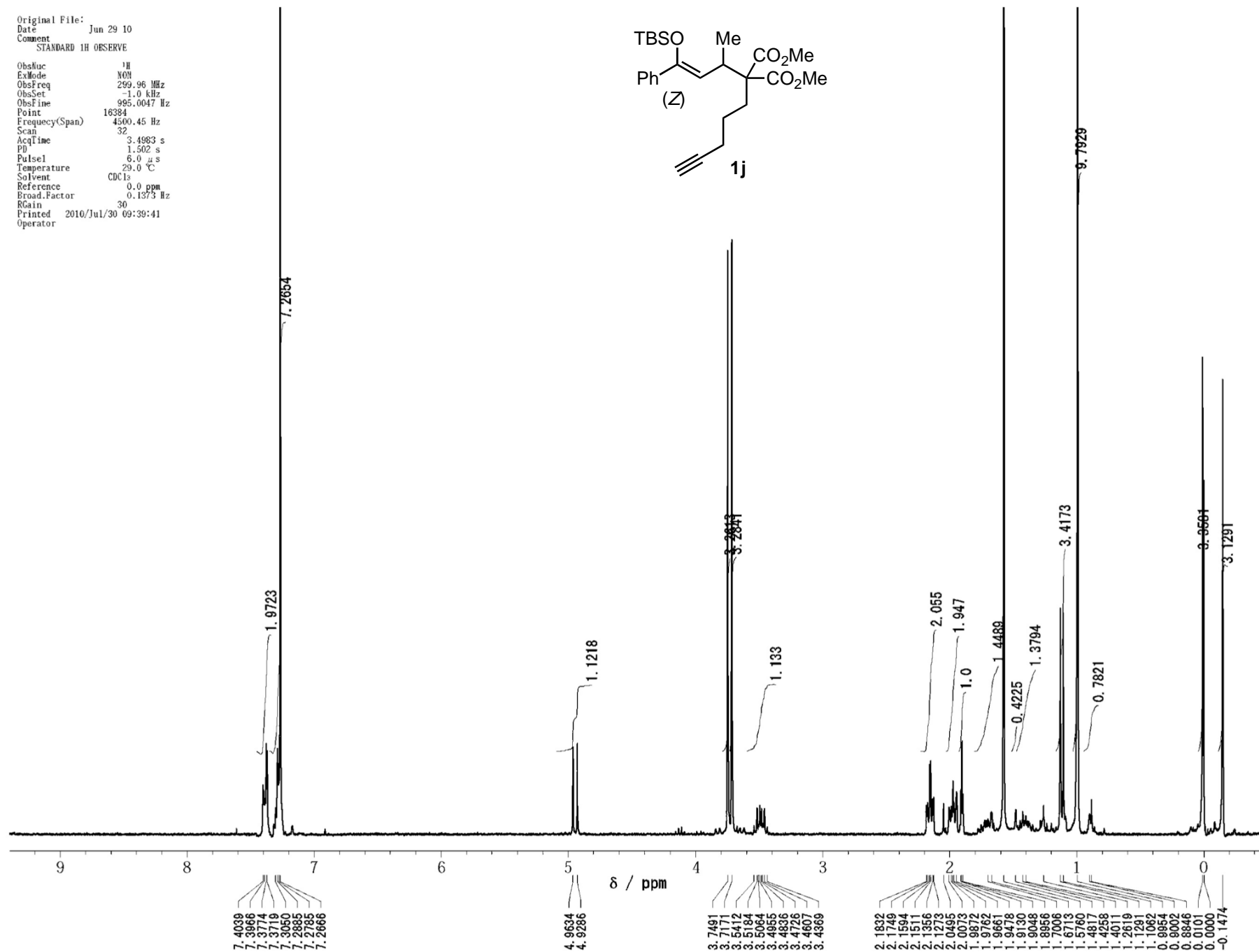
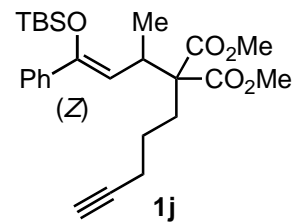


Original File:
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 Comment C13 Standard Observe
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 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 120
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 09:29:28
 Operator

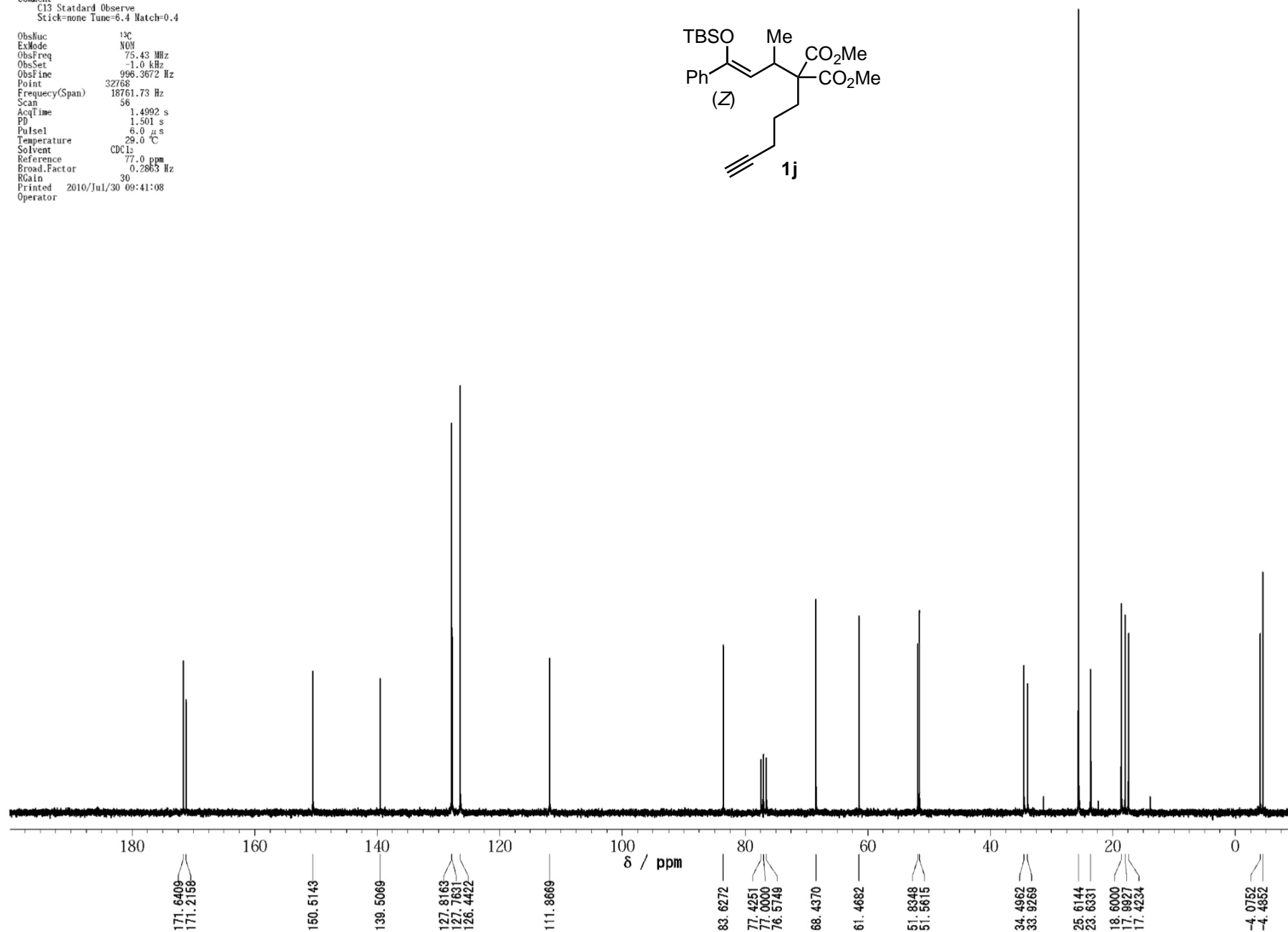
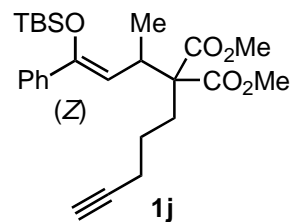


Original File:
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 ObsMod 1H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 30
 Printed 2010/Jul/30 09:39:41
 Operator



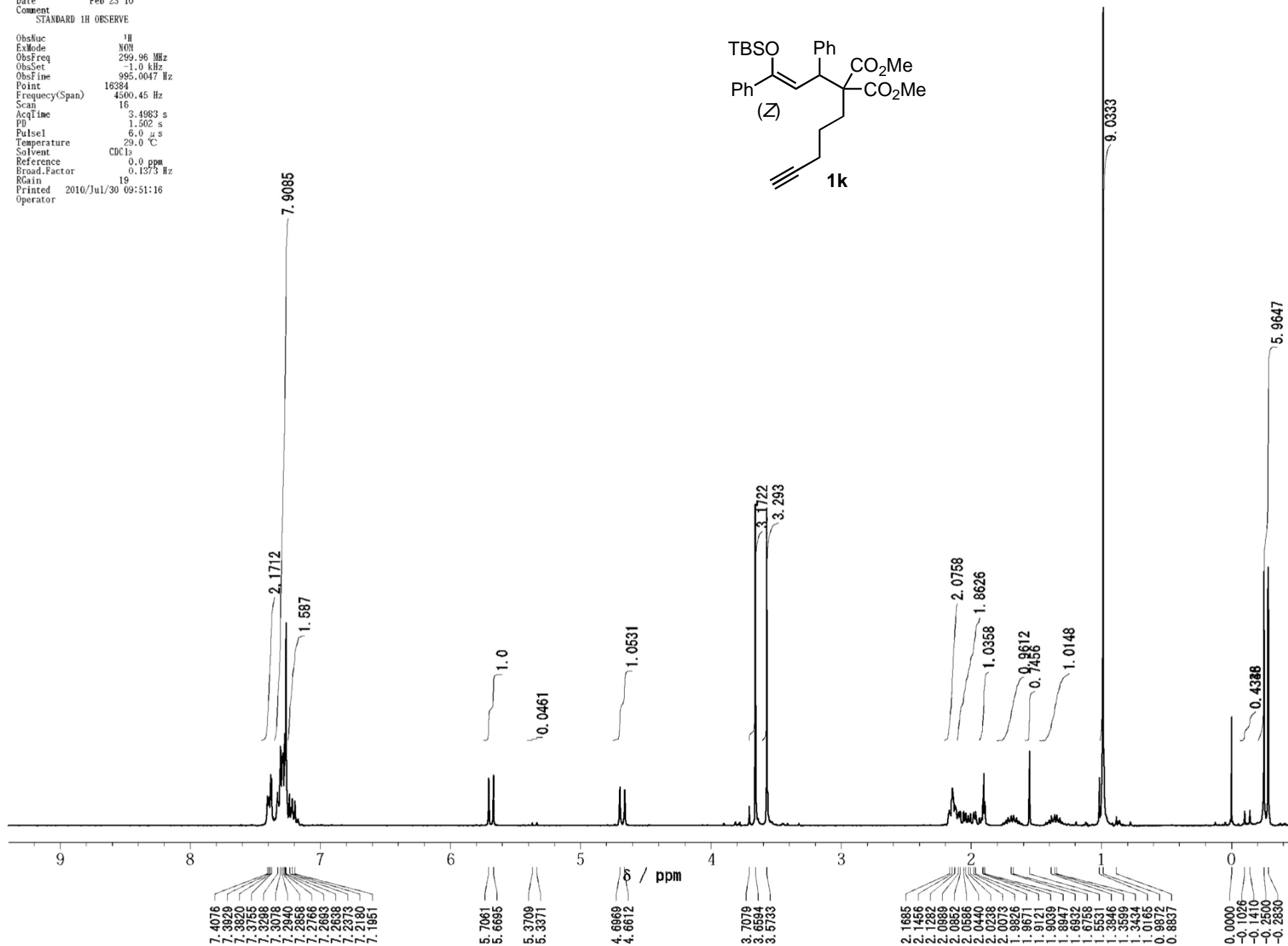
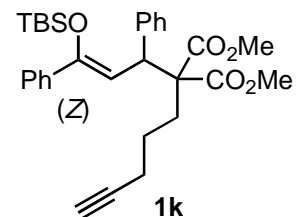
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 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
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 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 56
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
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 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 09:41:08
 Operator



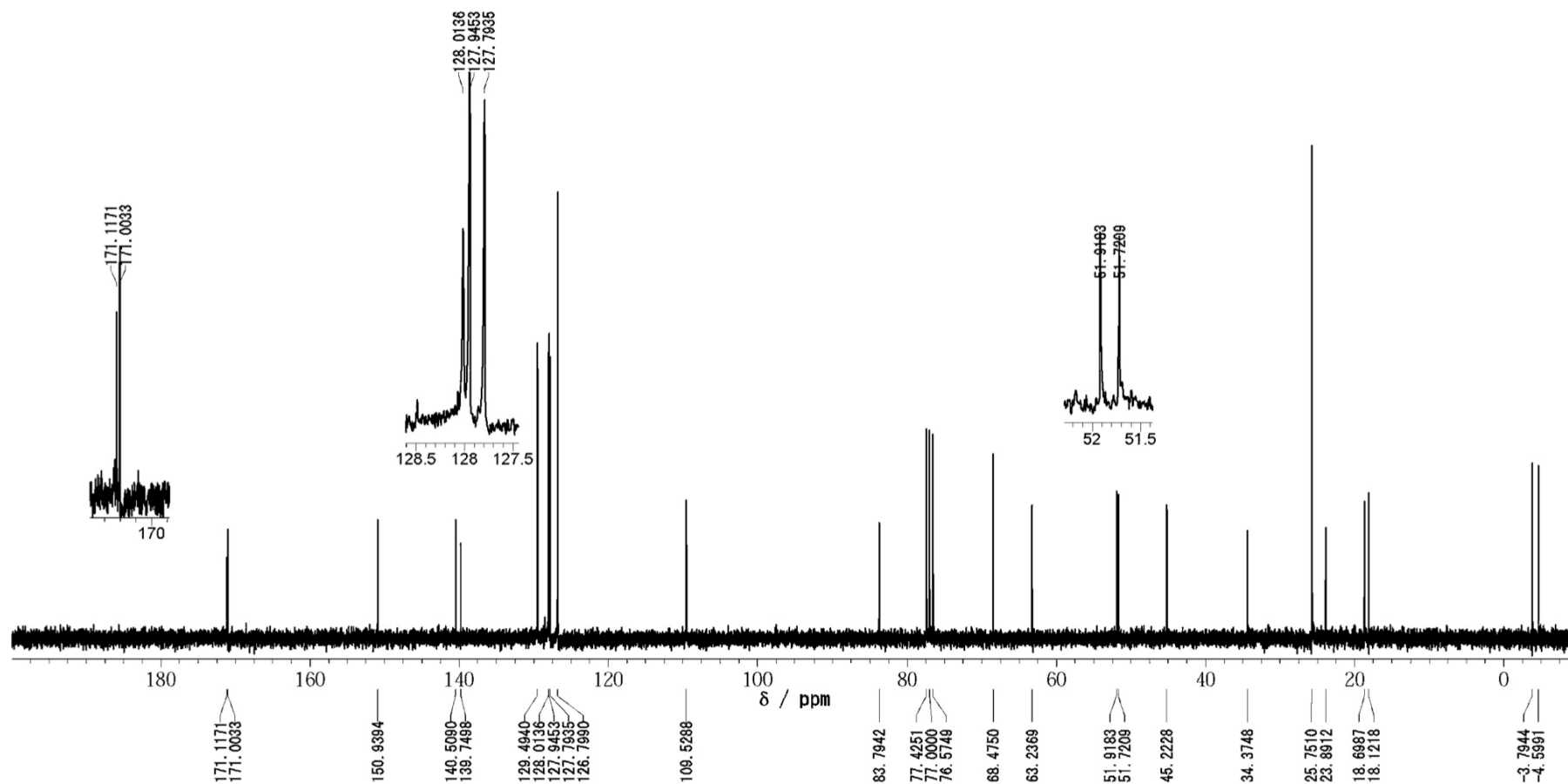
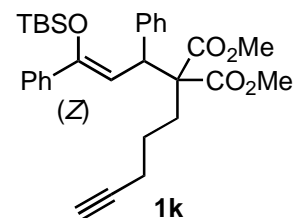
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Date Feb 23 10
Comment
STANDARD 1H OBSERVE

ObsMod 1H
ExMode NOE
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 16
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 19
Printed 2010/Jul/30 09:51:16
Operator

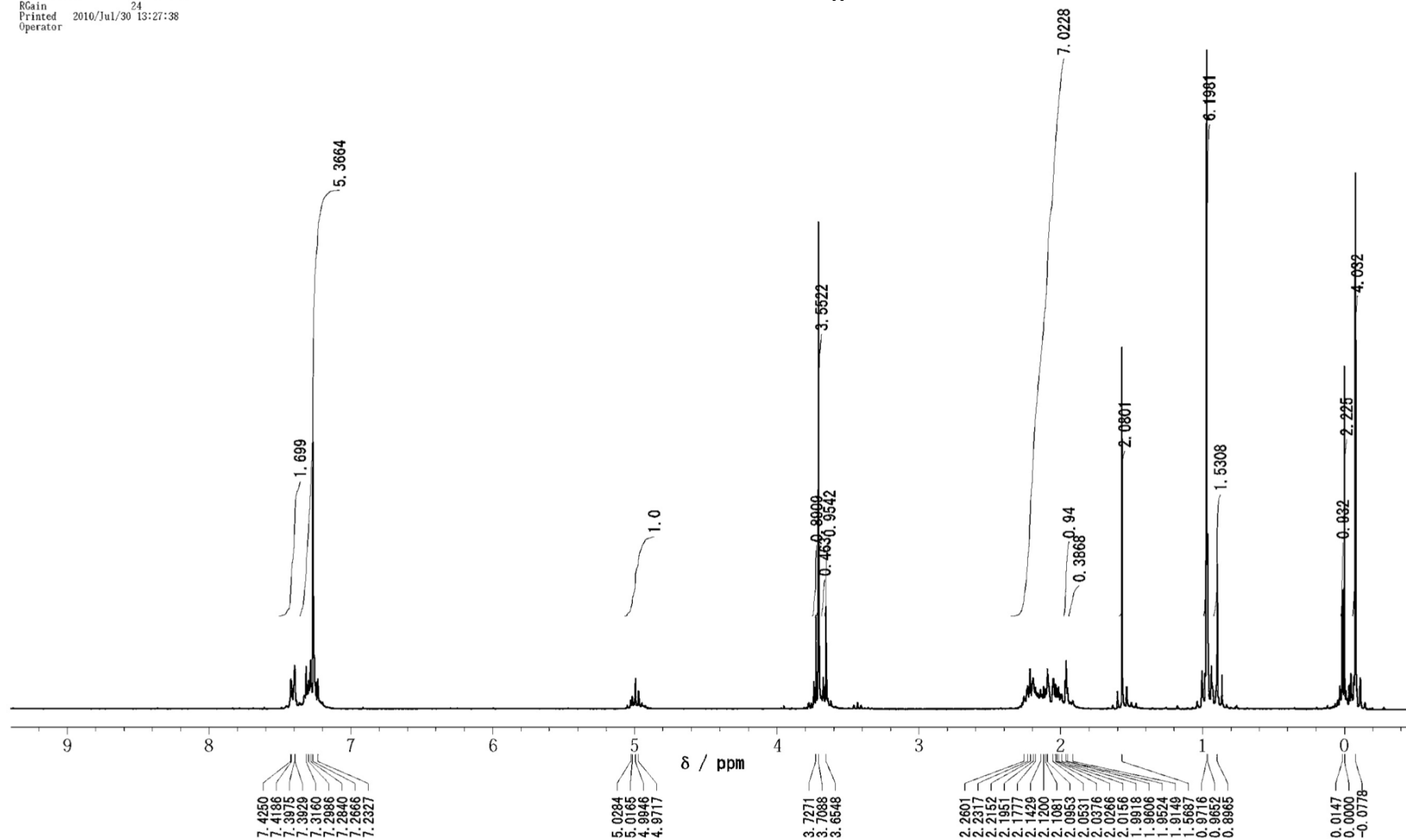
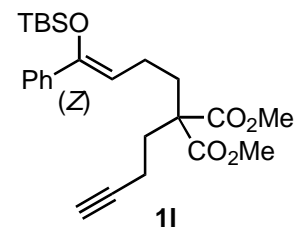


Original File:
 Date Feb 23 10
 Comment C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
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 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 96
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 09:53:43
 Operator

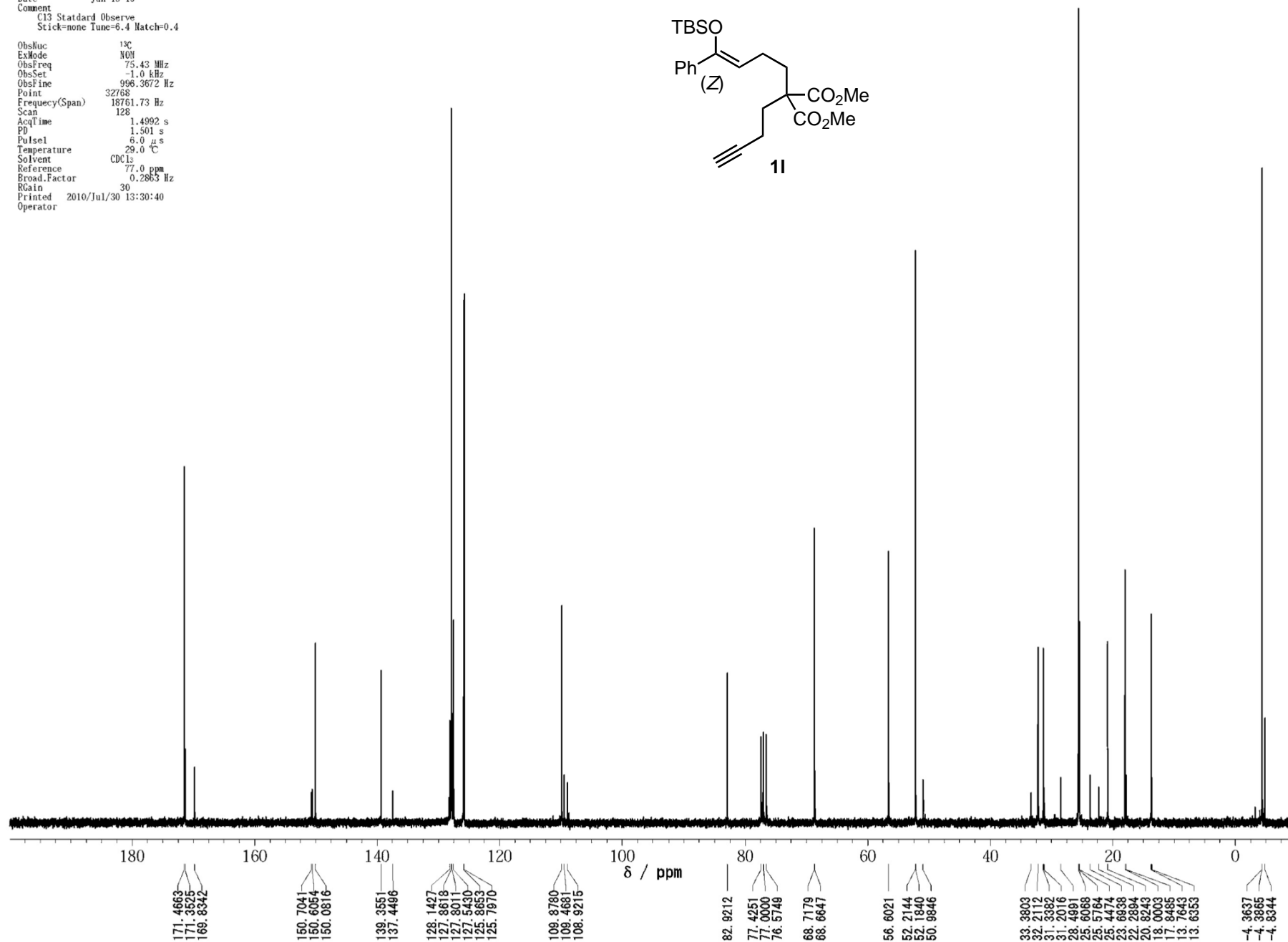
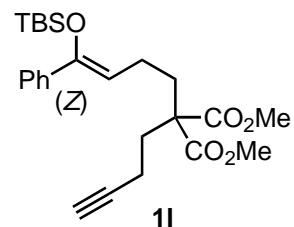


Original File:
 Date Jun 15 10
 Comment
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 ObsRuoc 1H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/30 13:27:38
 Operator

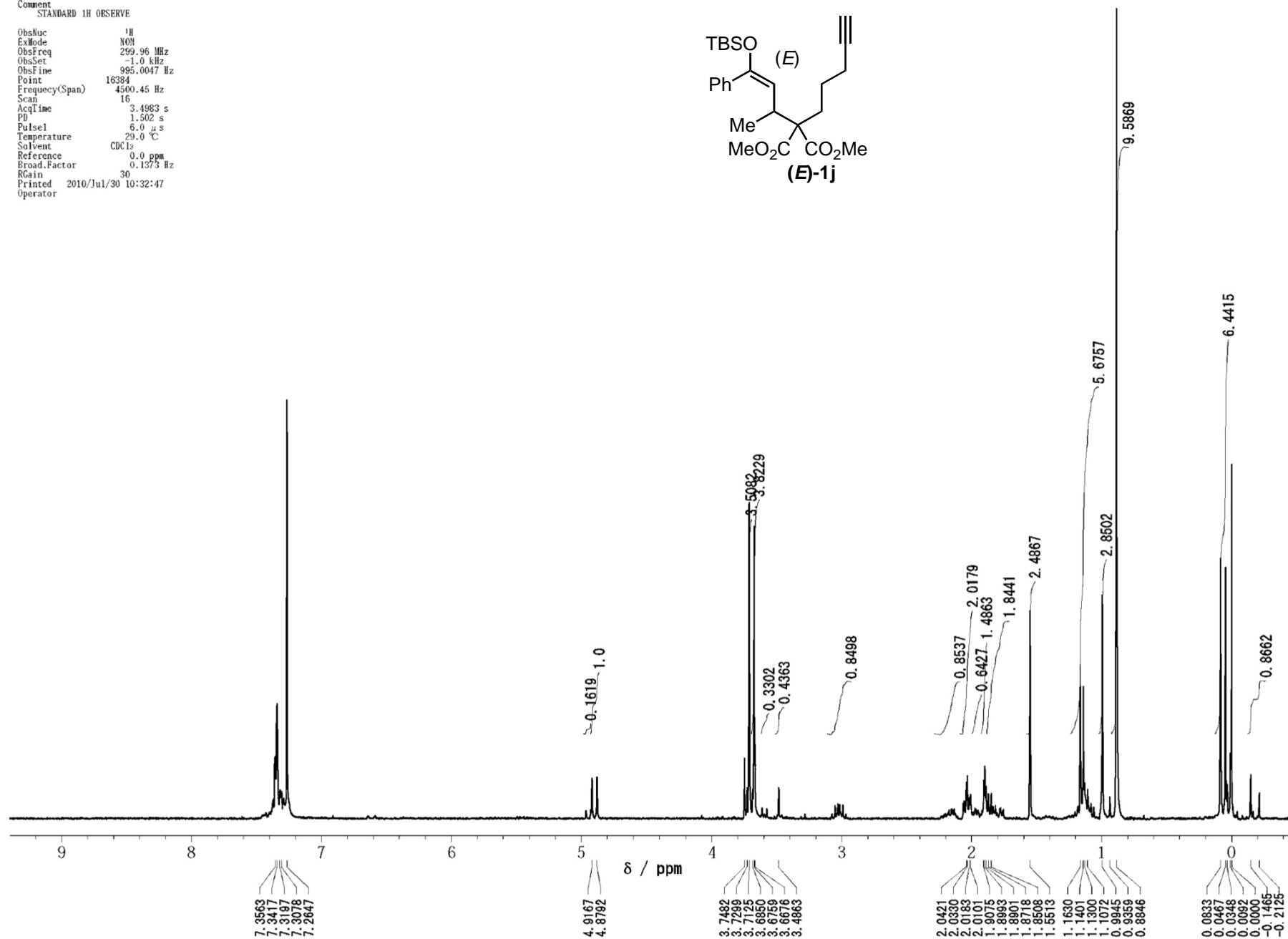
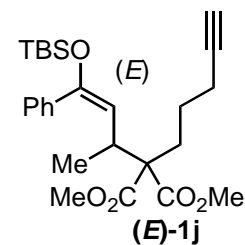


Original File:
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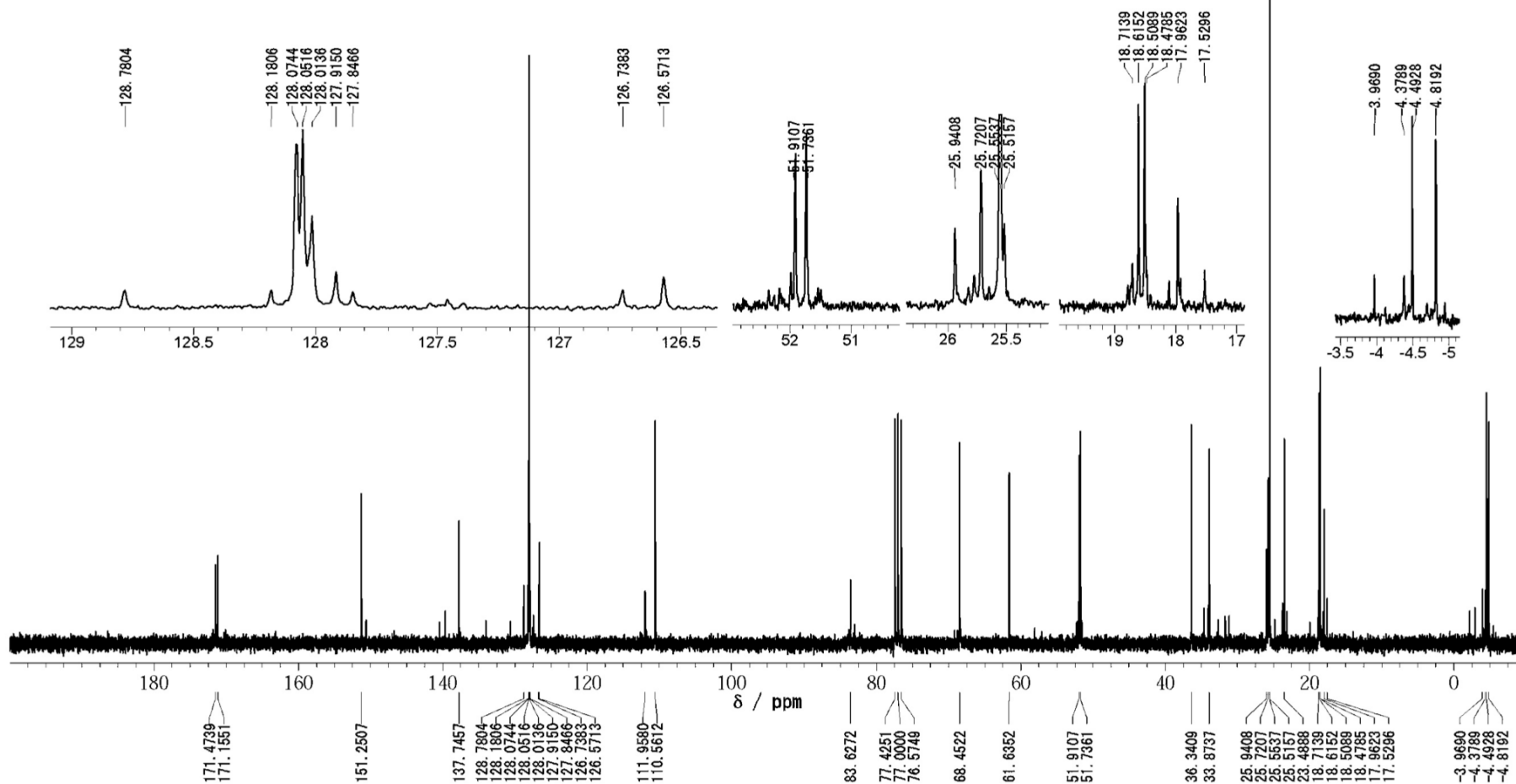
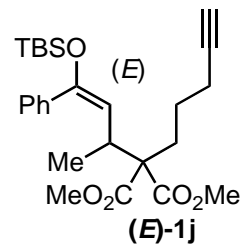
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 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 128
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 13:30:40
 Operator



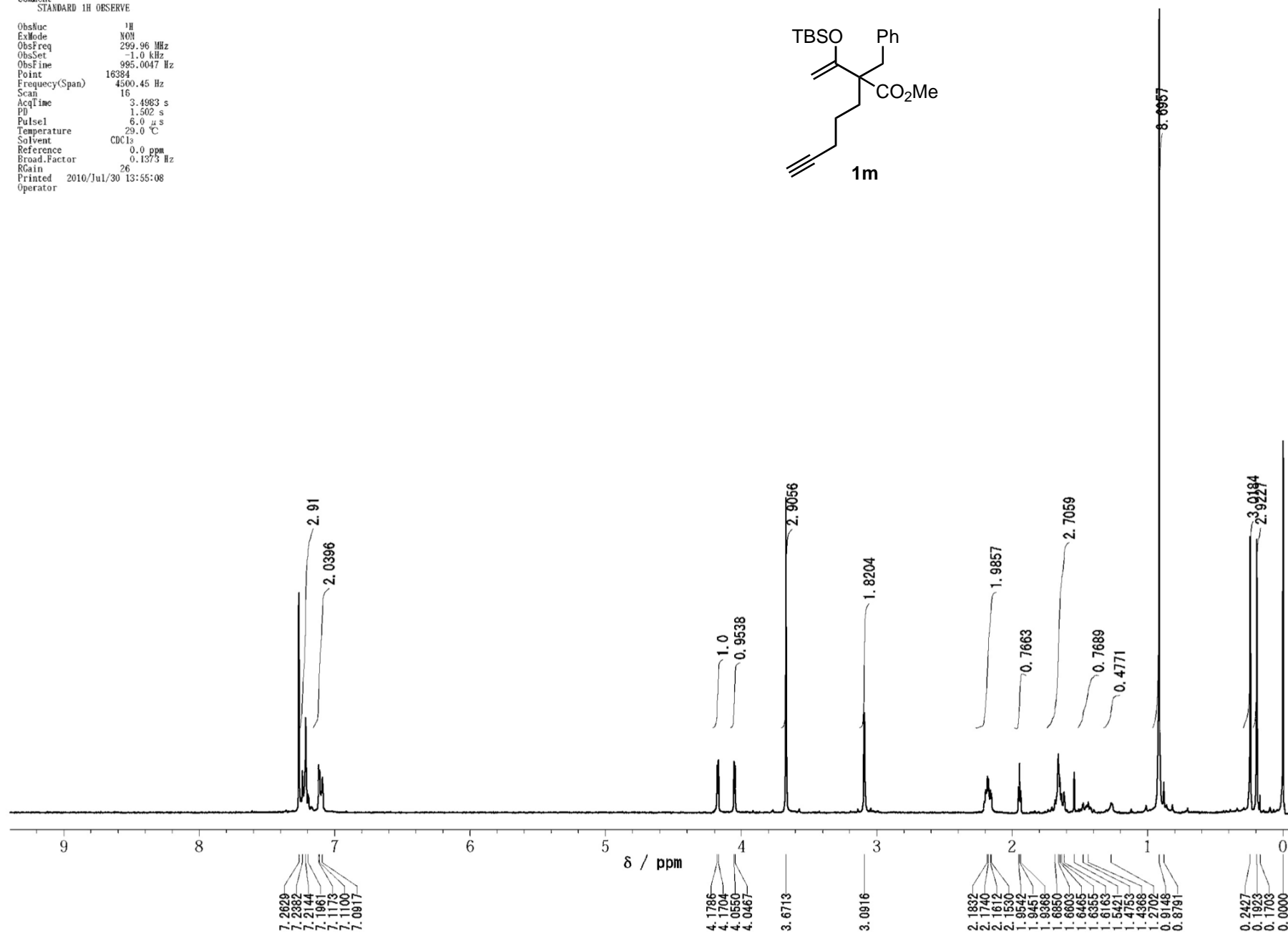
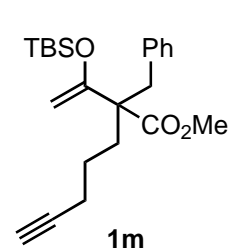
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 Date Feb 23 10
 Comment
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 ObsMod 1H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 16
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 30
 Printed 2010/Jul/30 10:32:47
 Operator



ObsIduc	13C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	1.0 kHz
ObsLine	996.3672 Hz
Point	32768
Frequency(Span)	18761.73 Hz
Scan	360
AcqTime	1.4992 s
PD	1.501 s
Pulse	6.0 μ s
Temperature	29.0 $^{\circ}$ C
Solvent	CDCl ₃
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2010/Jul/30 10:36:15
Operator	

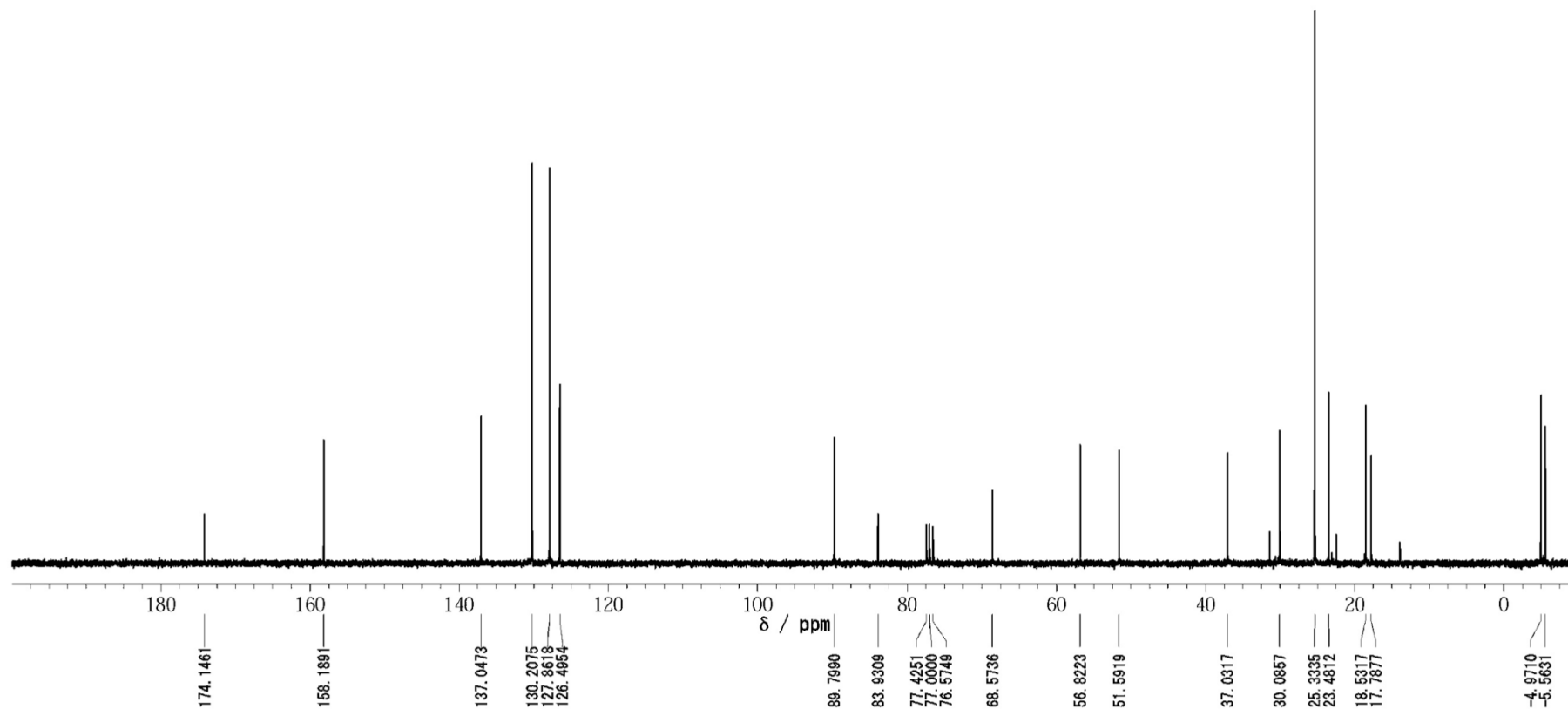
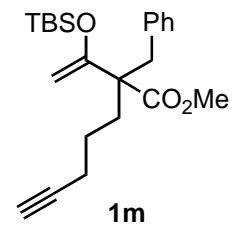


Original File:
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 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 16
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
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 Printed 2010/Jul/30 13:55:08
 Operator

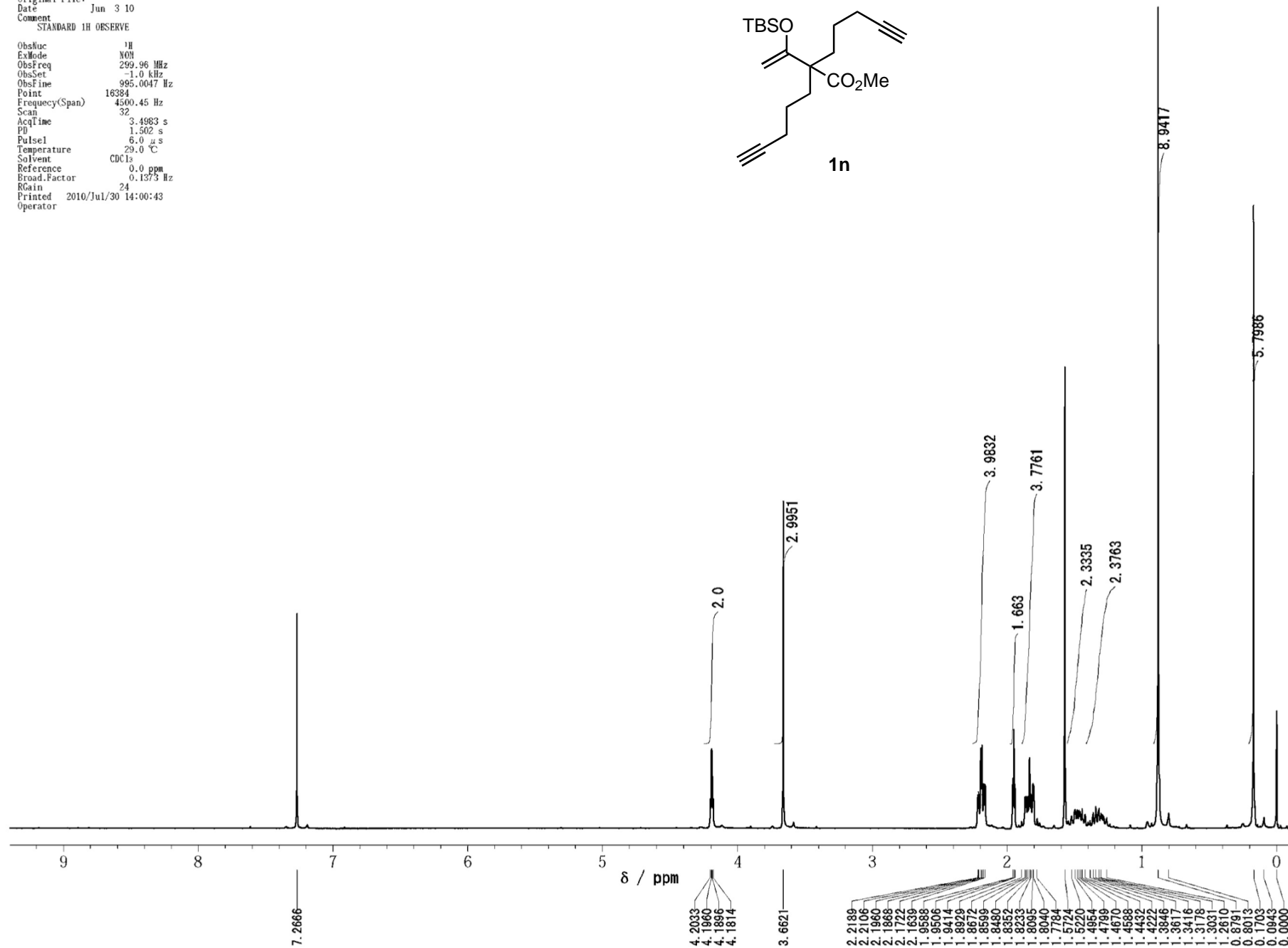
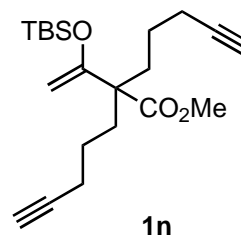


Original File:
 Date Apr 9 10
 Comment C13 Standard Observe
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 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 112
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
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 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 13:56:13
 Operator

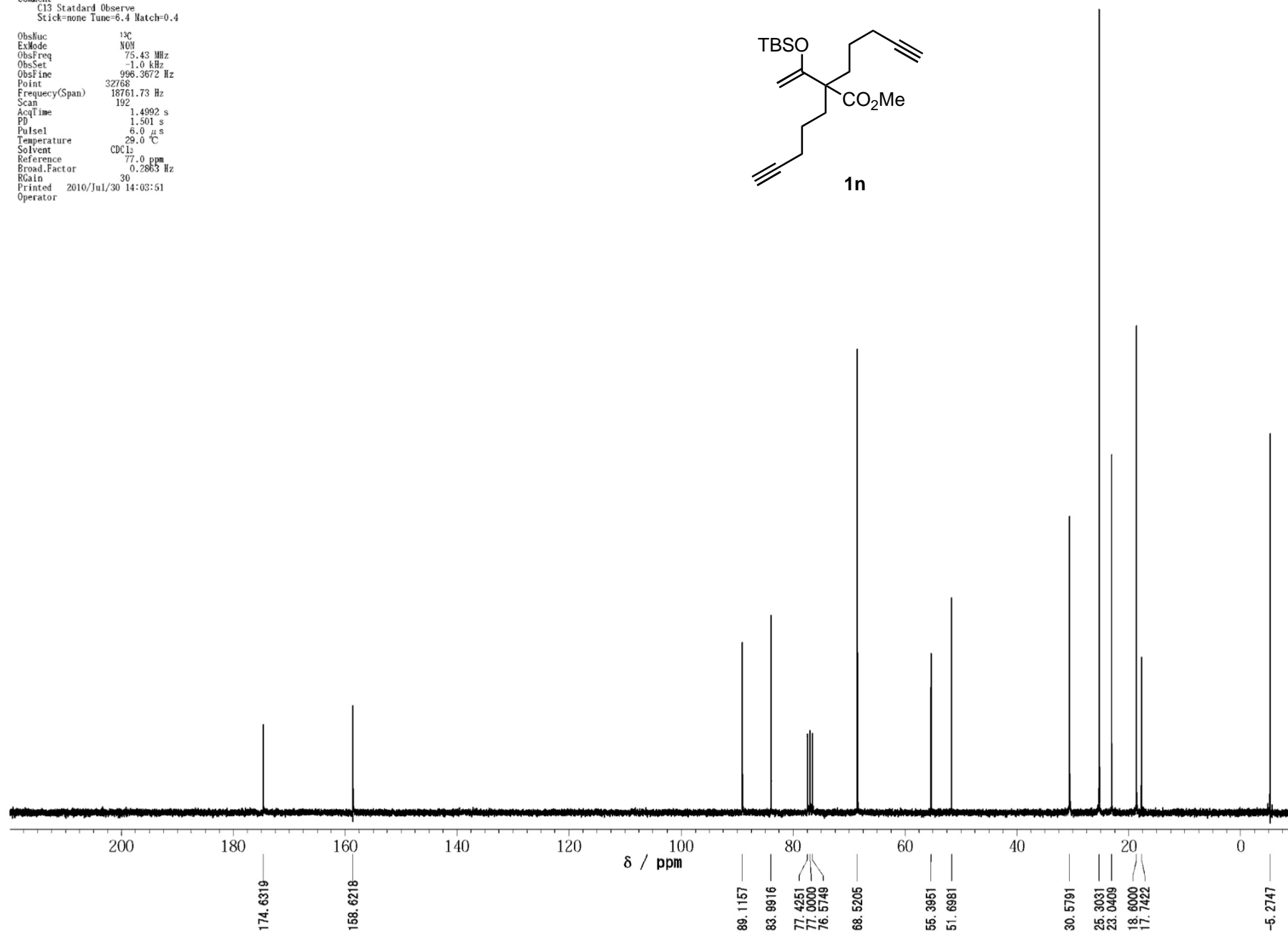
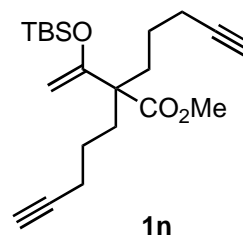


Original File: Jun 3 10
 Date
 Comment
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 ObsRuoc 1H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/30 14:00:43
 Operator



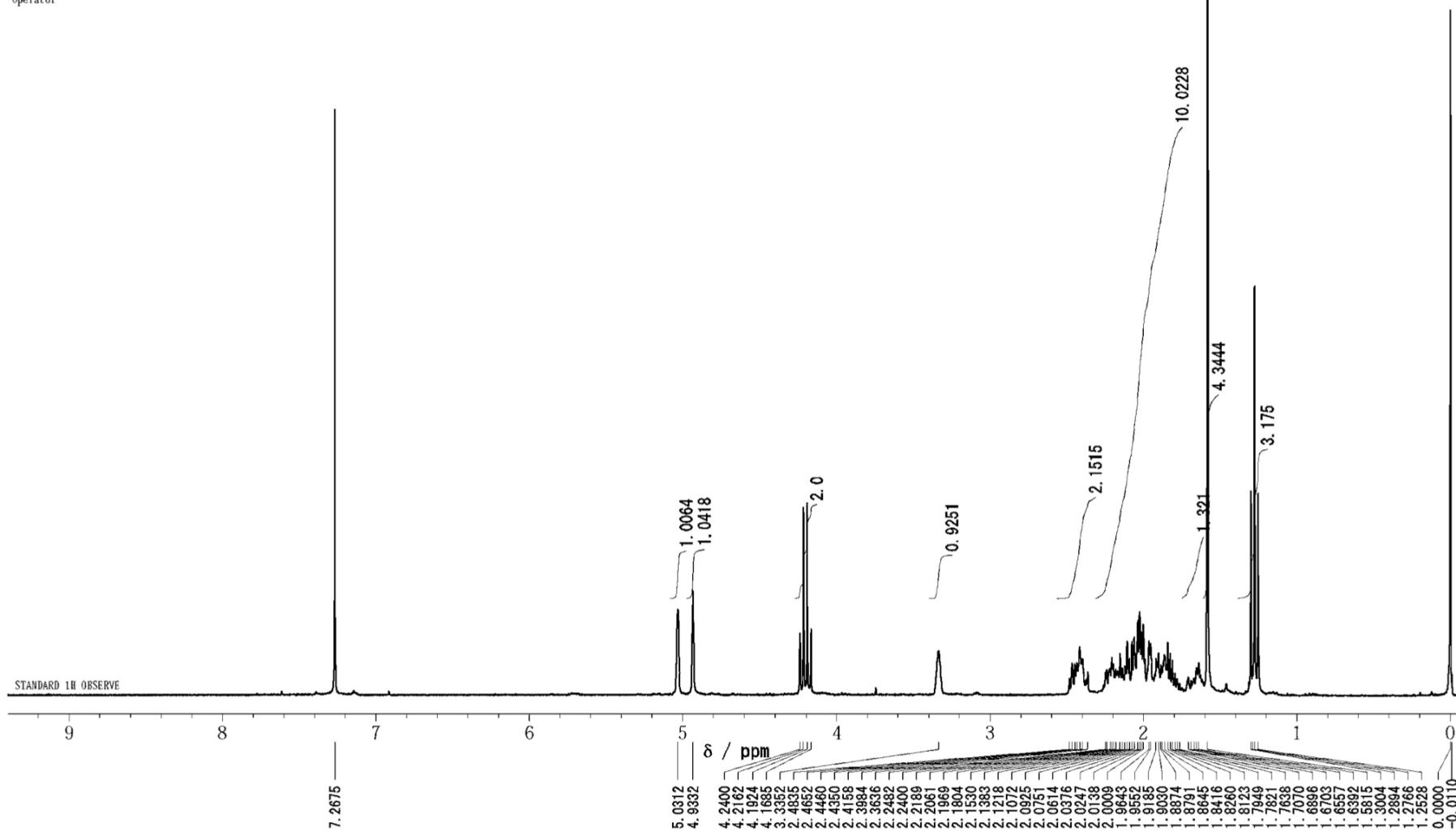
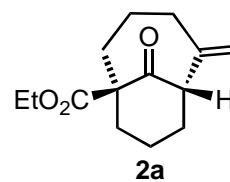
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 Date
 Comment C13 Standard Observe
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ObsRoc 13C
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 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 192
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 14:03:51
 Operator



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 Original File:
 Date Jun 21 10
 Comment
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ObsNuc 1H
 ExMode NON
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 29
 Printed 2010/Jul/29 21:07:42
 Operator



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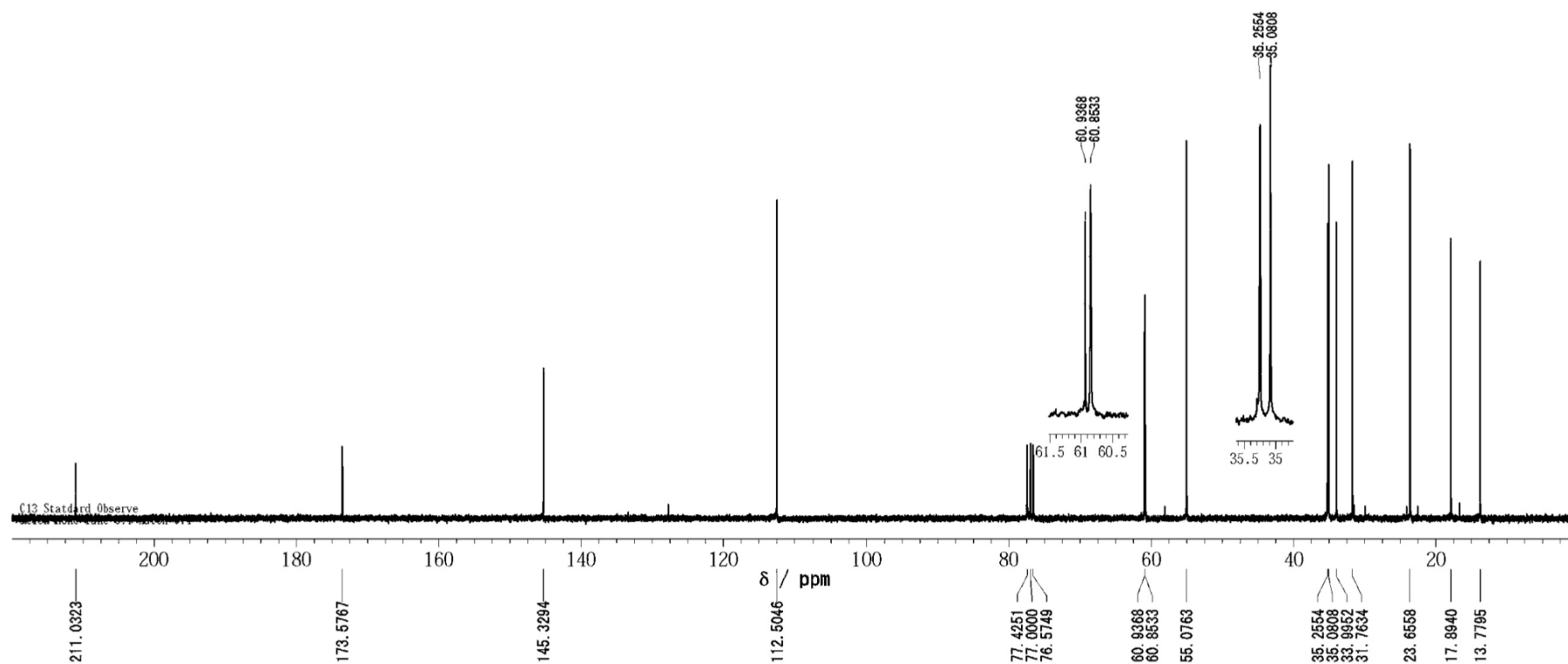
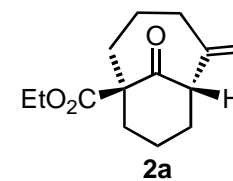
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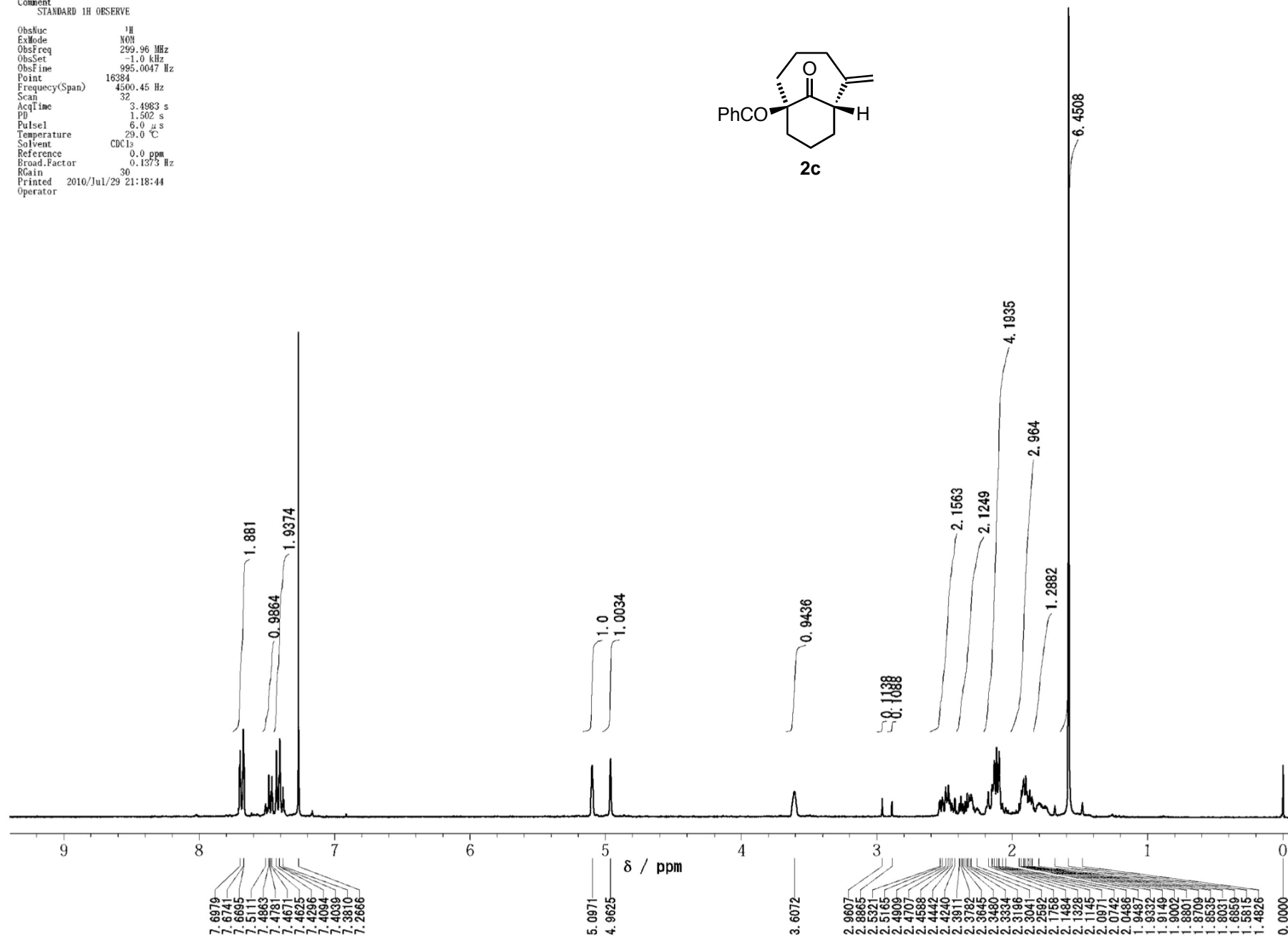
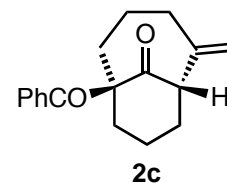
C13 Standard Observe

Stick:none Tune=6.4 Match=0.4

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ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequency(Span) 18761.73 Hz
Scan 160
AcqTime 1.4892 s
PD 1.501 s
Pulse1 6.0 μ s
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Solvent CDCl₃
Reference 77.0 ppm
Broad.Factor 0.2865 Hz
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Printed 2010/Jul/29 21:09:21
Operator

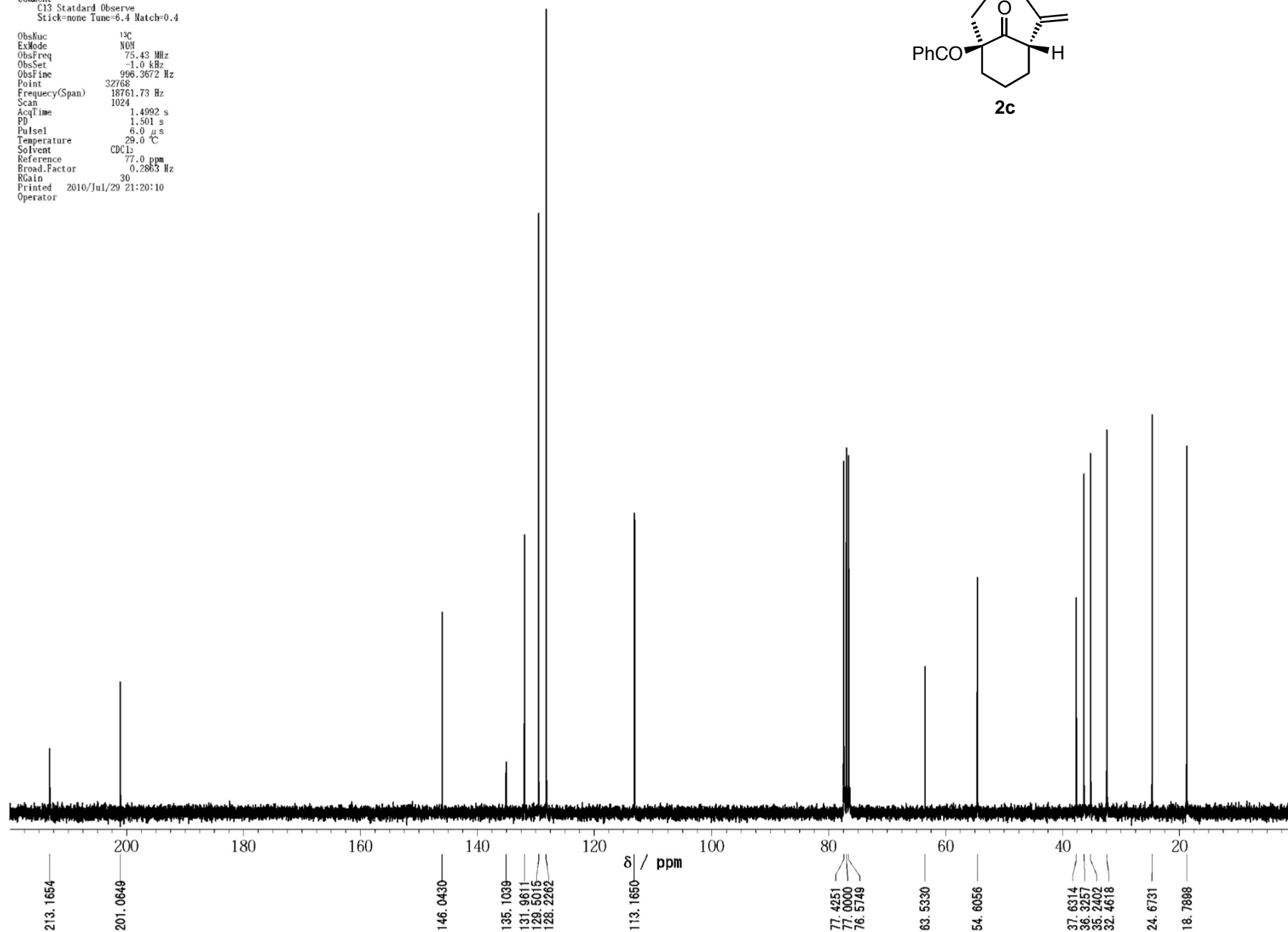
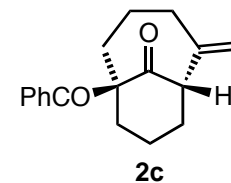


Original File: Jul 2 10
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 ExMode: NMR
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 ObsSet: -1.0 kHz
 ObsFine: 995.0047 Hz
 Point: 16384
 Frequency(Span): 4500.45 Hz
 Scan: 32
 AcqTime: 3.4983 s
 PD: 1.502 s
 Pulse1: 6.0 μ s
 Temperature: 29.0 $^{\circ}$ C
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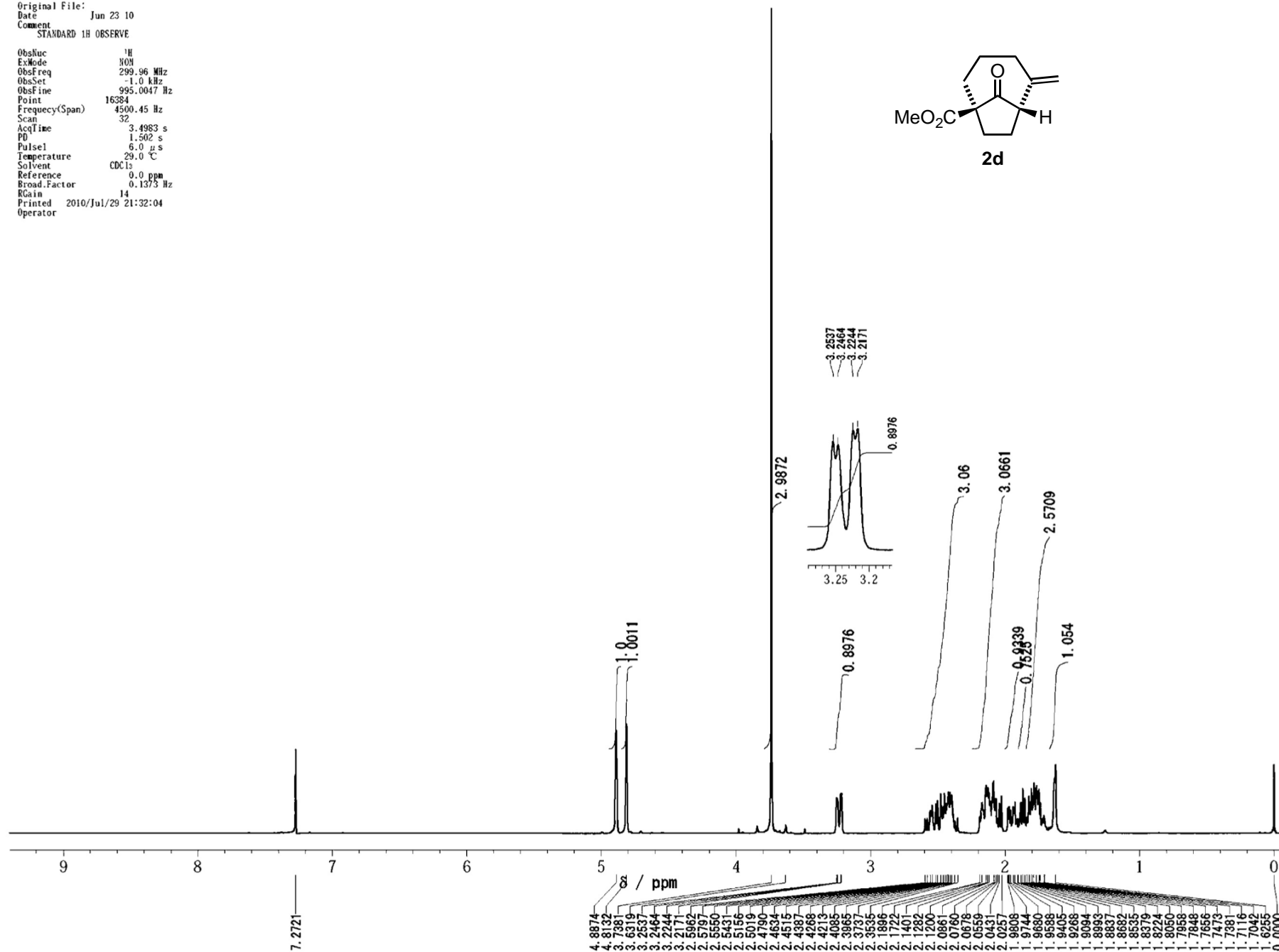
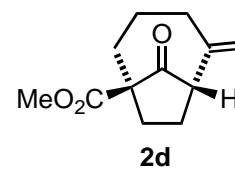
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 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 1024
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
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 Broad.Factor 0.2863 Hz
 RGain 30
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 Operator



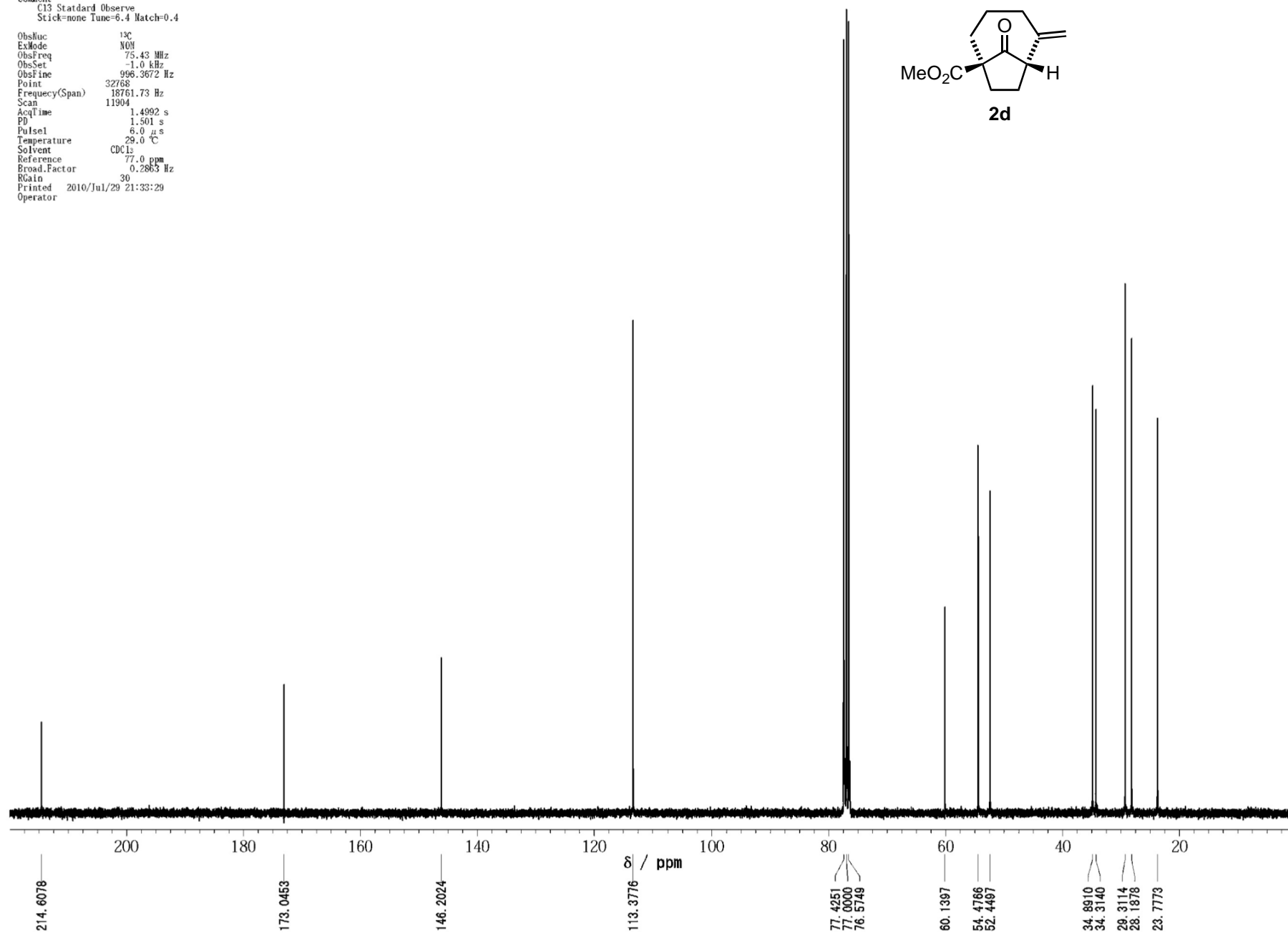
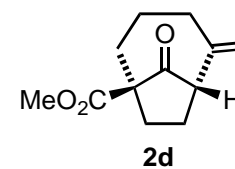
Original File: Jun 23 10
 Date
 Comment
 STANDARD 1H OBSERVE

ObsRuoc ¹H
 ExMode 108
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 14
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 Operator

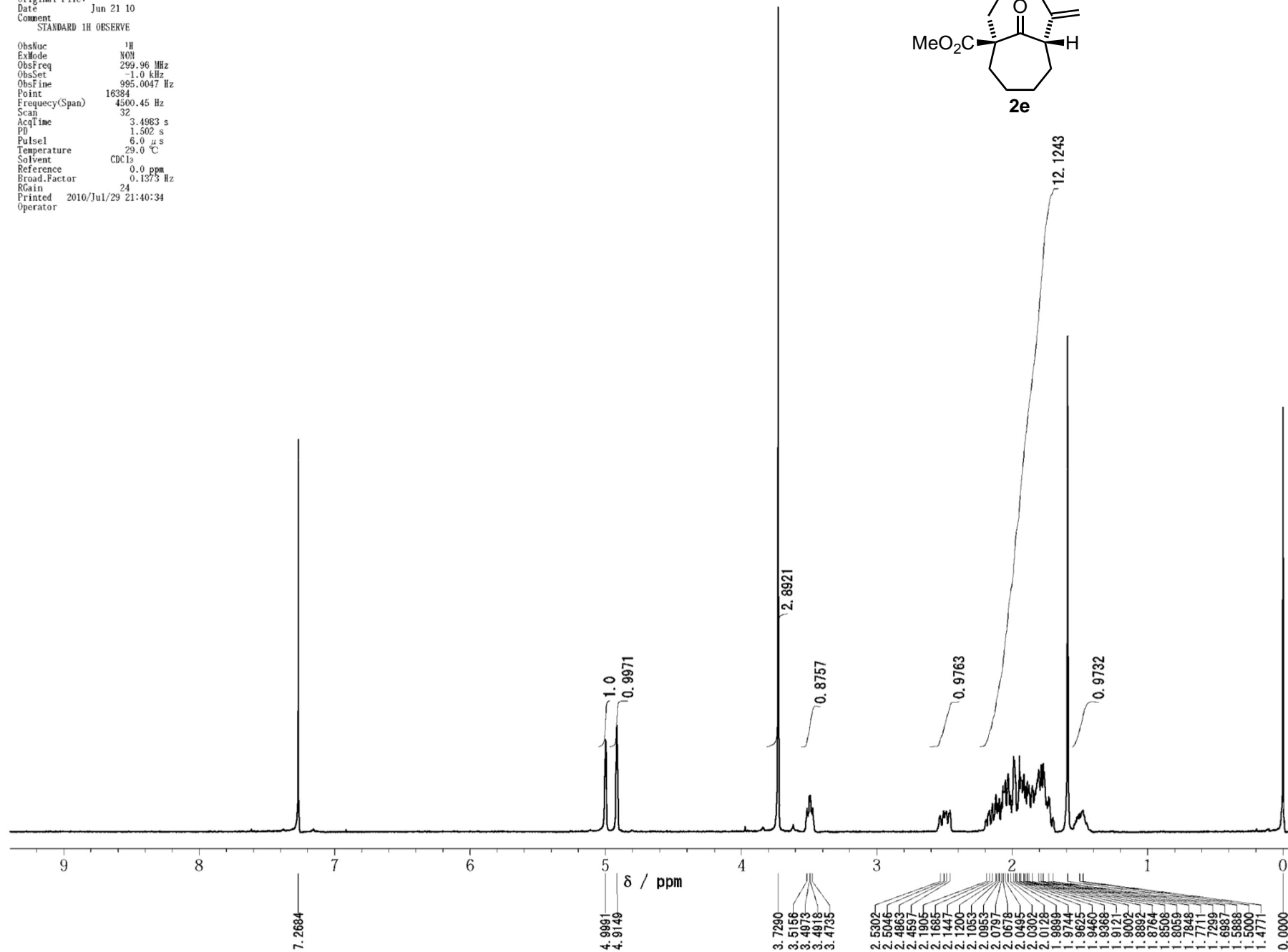
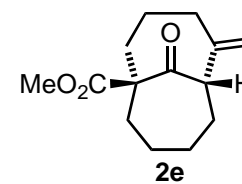


Original File:
 Date Jun 23 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

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 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 11904
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
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 Solvent CDCl₃
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 Broad.Factor 0.2863 Hz
 RGain 30
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 Operator

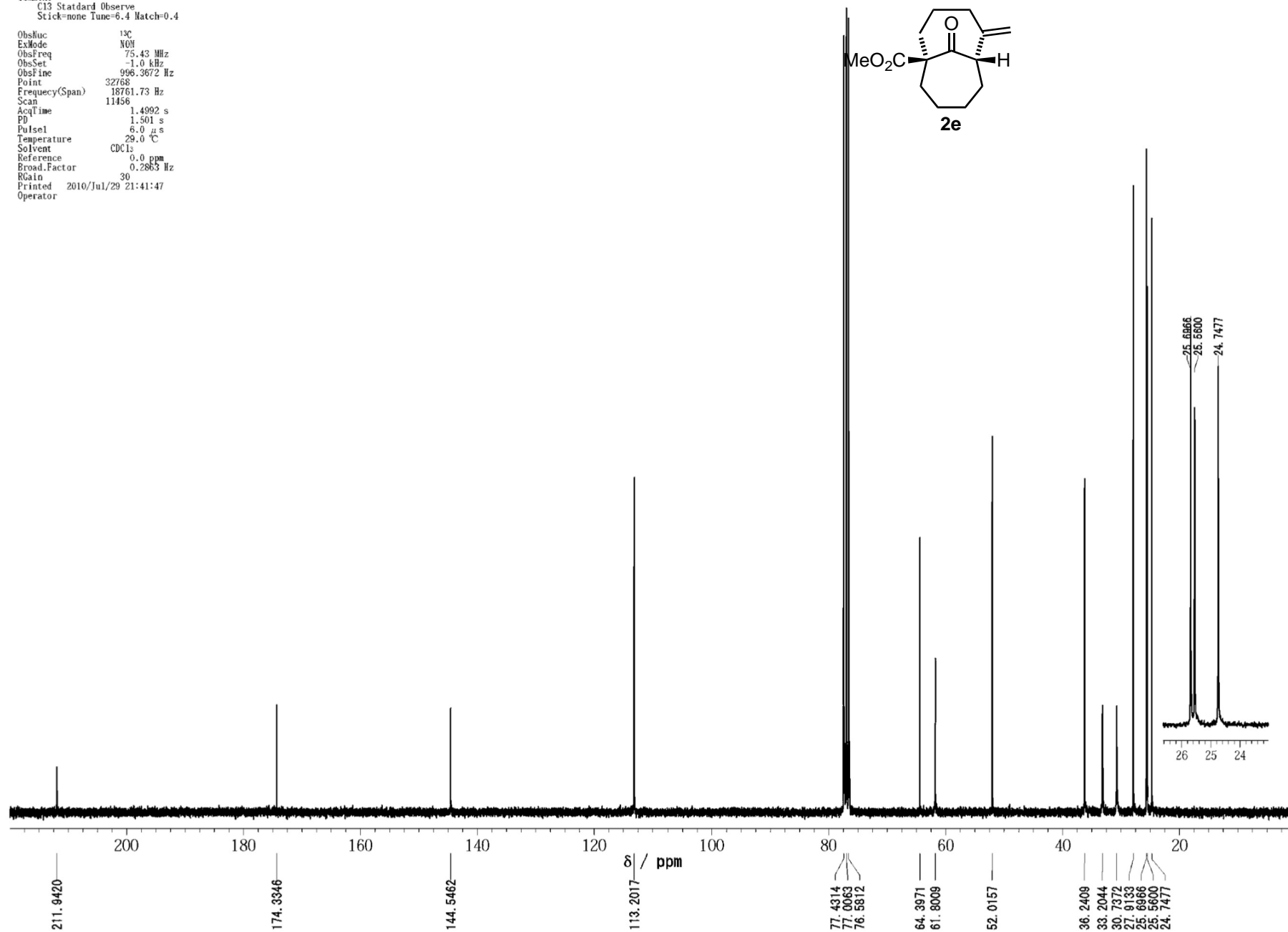
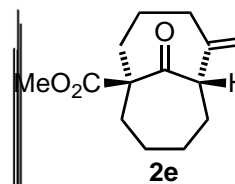


Original File:
 Date Jun 21 10
 Comment
 STANDARD 1H OBSERVE
 ObsRuoc ¹H
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 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
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 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
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 Broad.Factor 0.1373 Hz
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 Operator



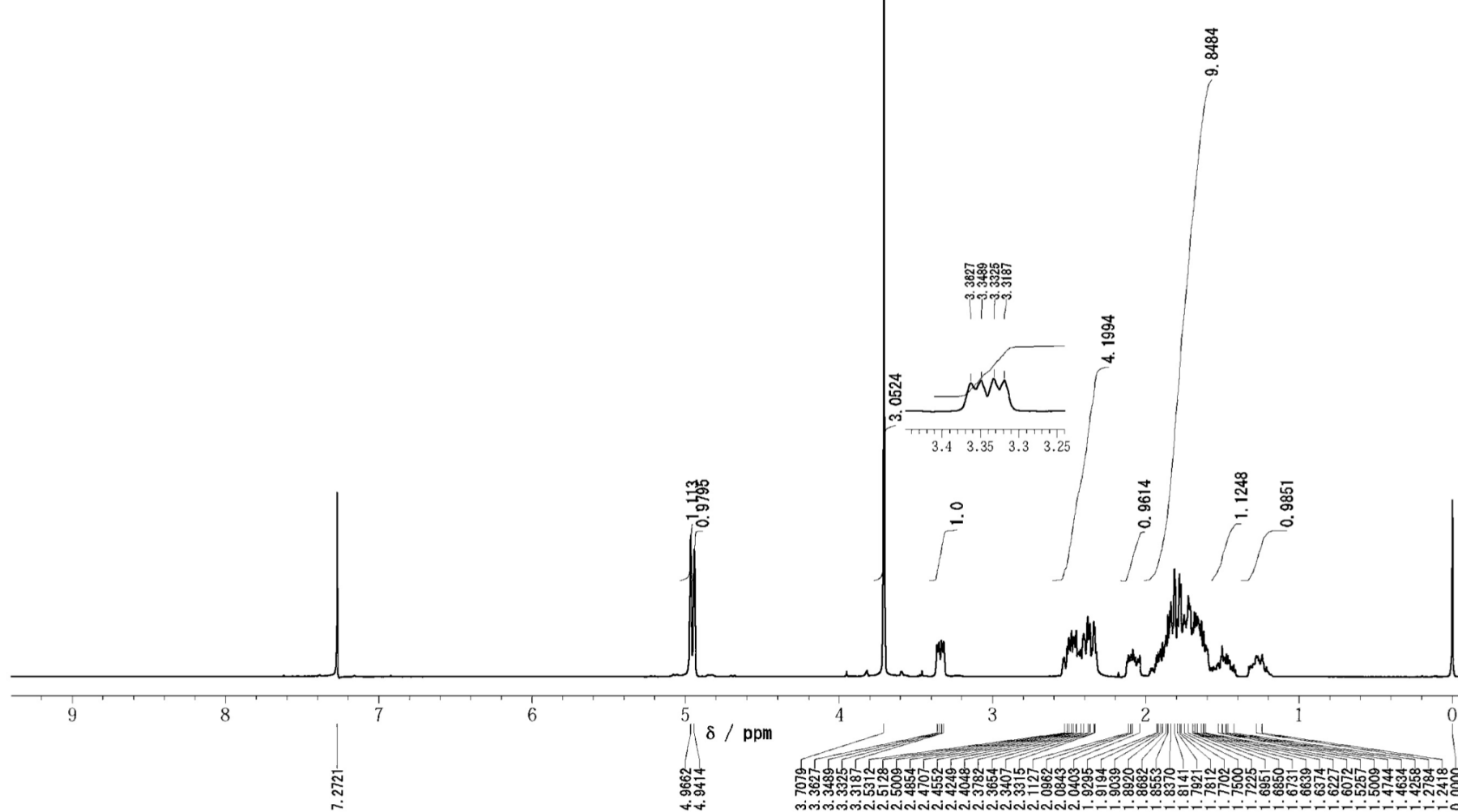
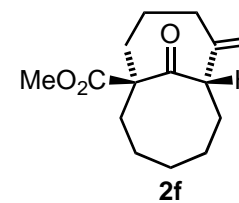
Original File:
 Date Jun 21 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 11456
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 21:41:47
 Operator



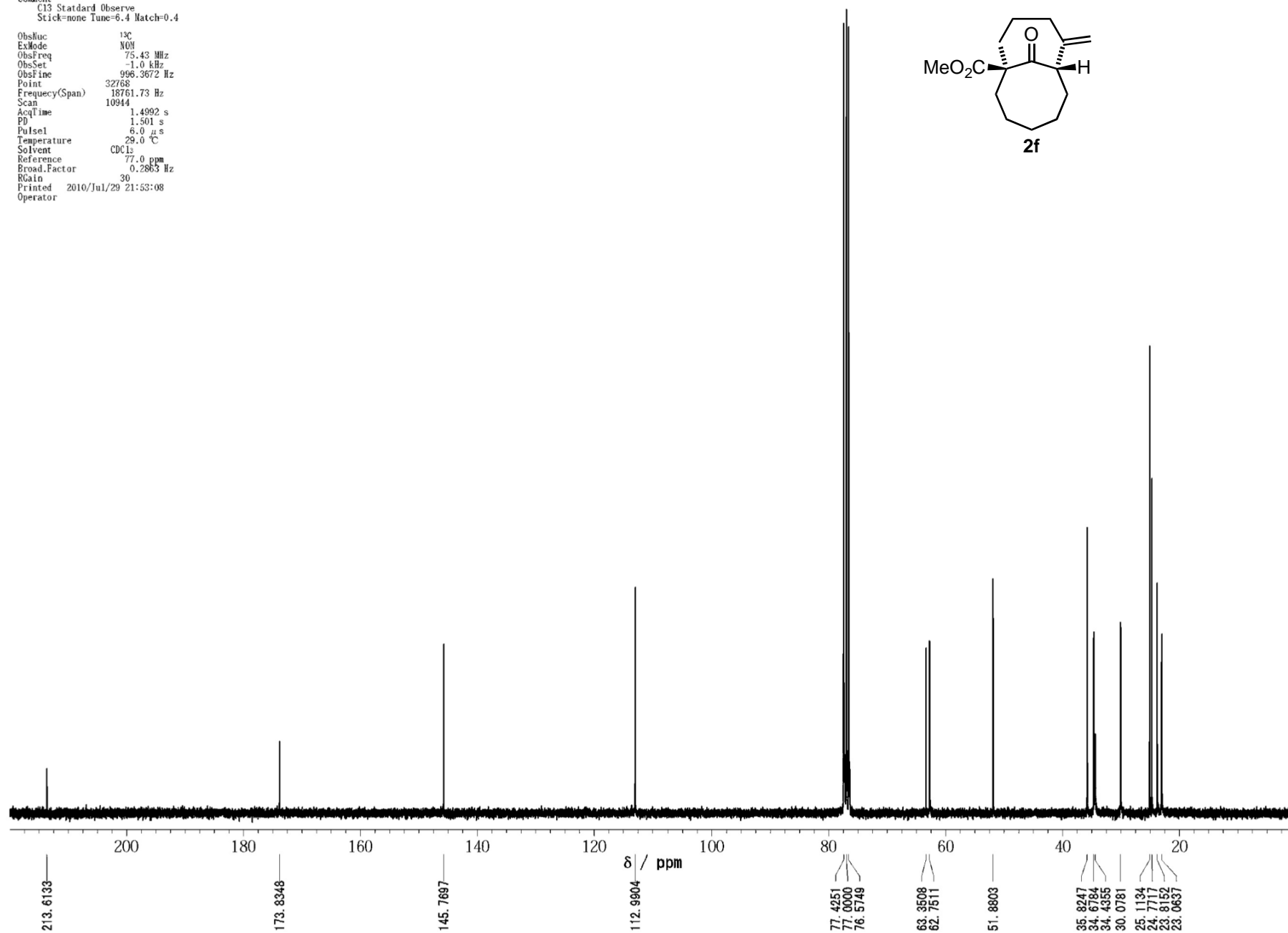
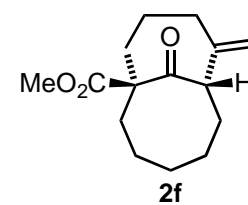
Original File:
Date Jul 3 10
Comment
STANDARD 1H OBSERVE

ObsRuoc 1H
ExMode NMR
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 13
Printed 2010/Jul/29 21:50:49
Operator



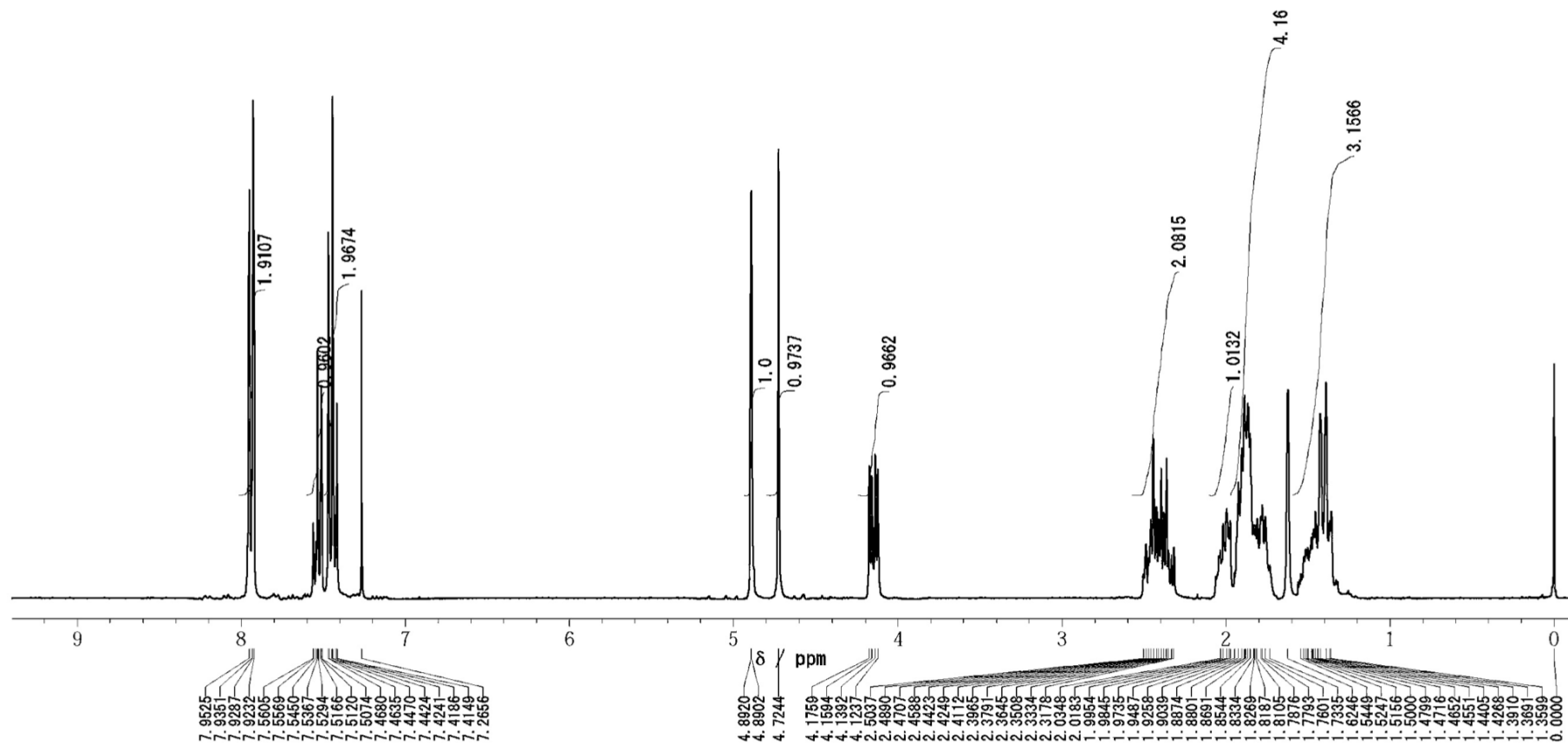
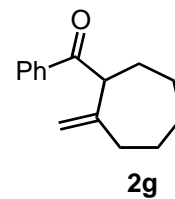
Original File:
 Date Jul 3 10
 Comment C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 10944
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 21:53:08
 Operator



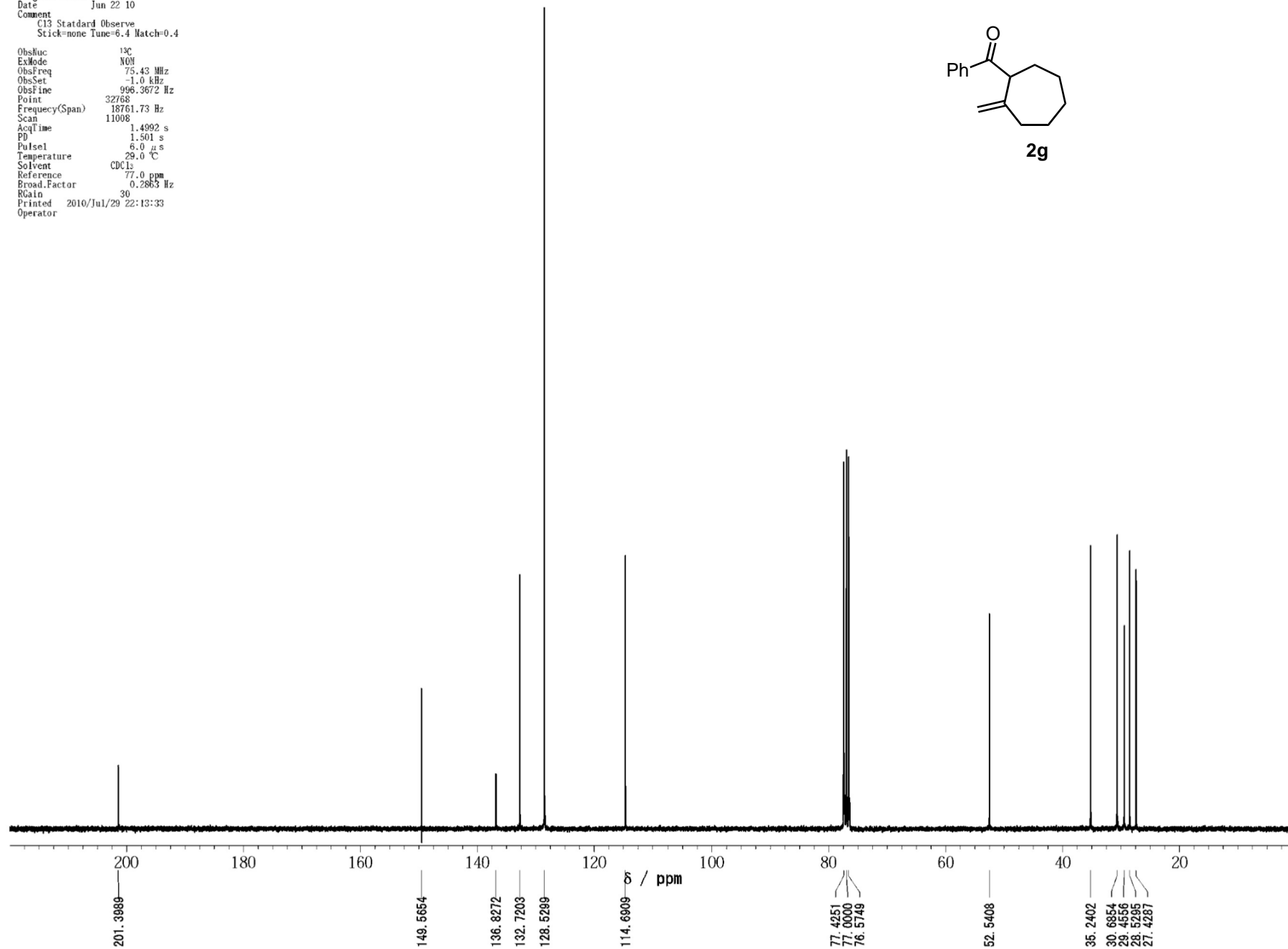
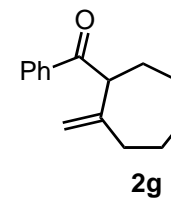
Original File:
Date Jun 22 10
Comment
STANDARD 1H OBSERVE

ObsRuoc ¹H
ExMode NMR
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 17
Printed 2010/Jul/29 22:12:07
Operator

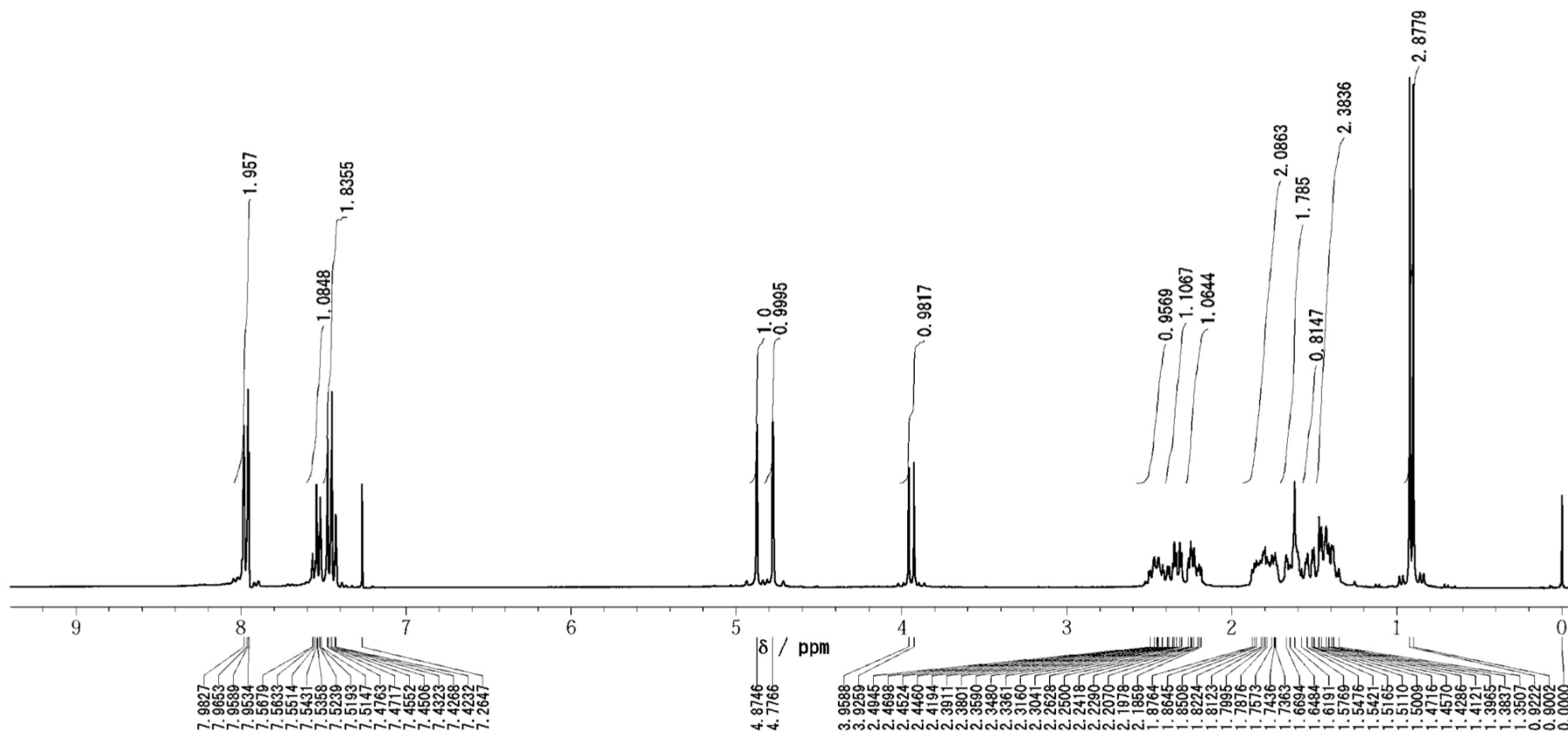
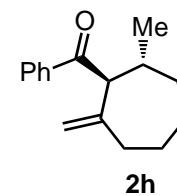


Original File:
 Date Jun 22 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
 ExMode N0H
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 11008
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 22:13:33
 Operator

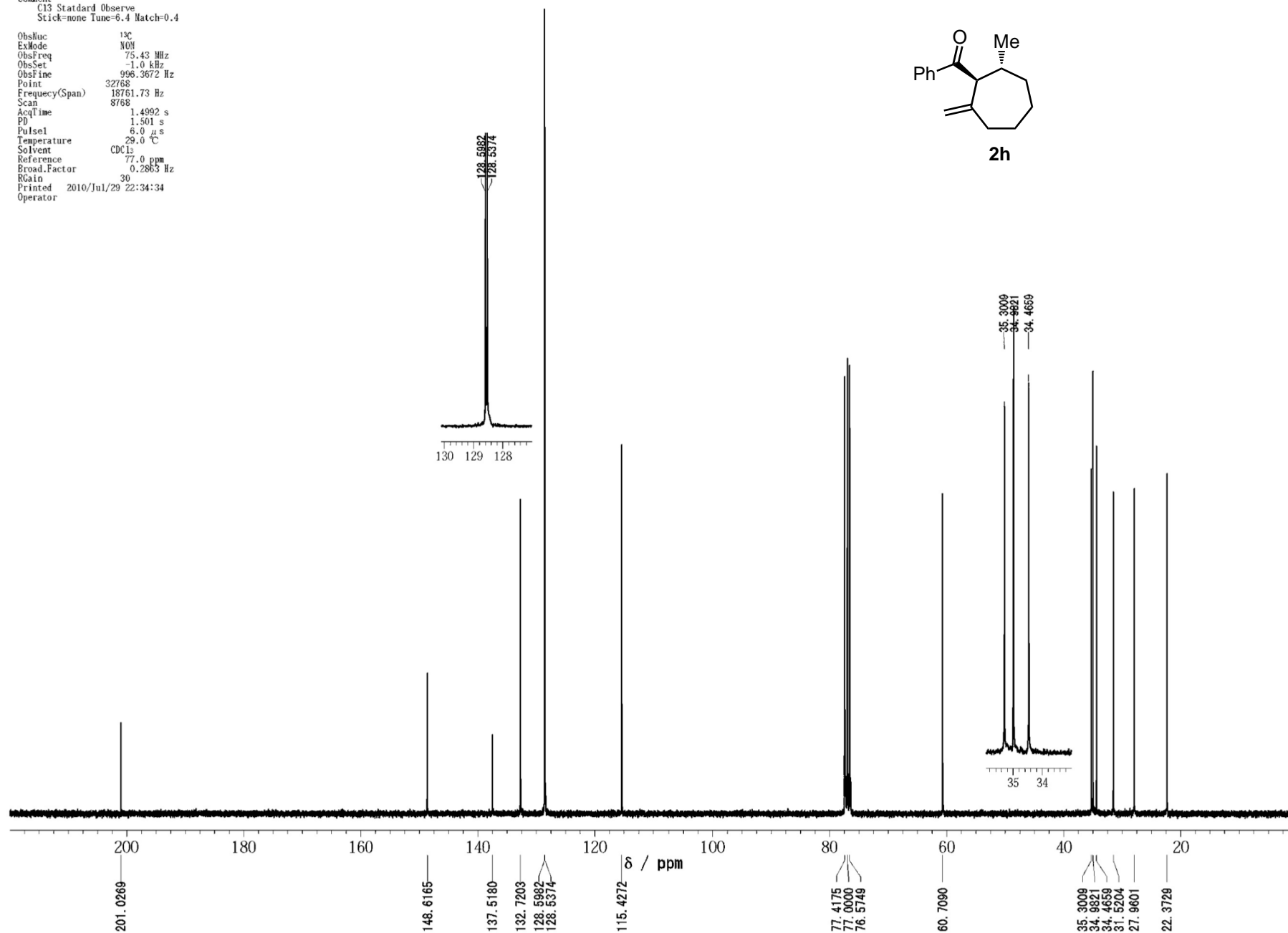
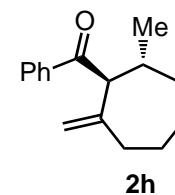


Obsluc		¹ H
ExMod		NH
ObsFreq	299.96	MHz
ObsSet	-1.0	kHz
ObsFreq	995.0047	Mz
Frequency(Span)	4500.45	Hz
Scan	32	
AcqTime	3.4983	s
PD	1.502	s
Pulse1	6.0	μs
Temperature	29.0	°C
Solvent	CDCl ₃	
Reference	0.0	ppm
Broad.Factor	0.1373	Hz
RGain	12	
Printed	2010/Jul/29	22:33:17
Operator		

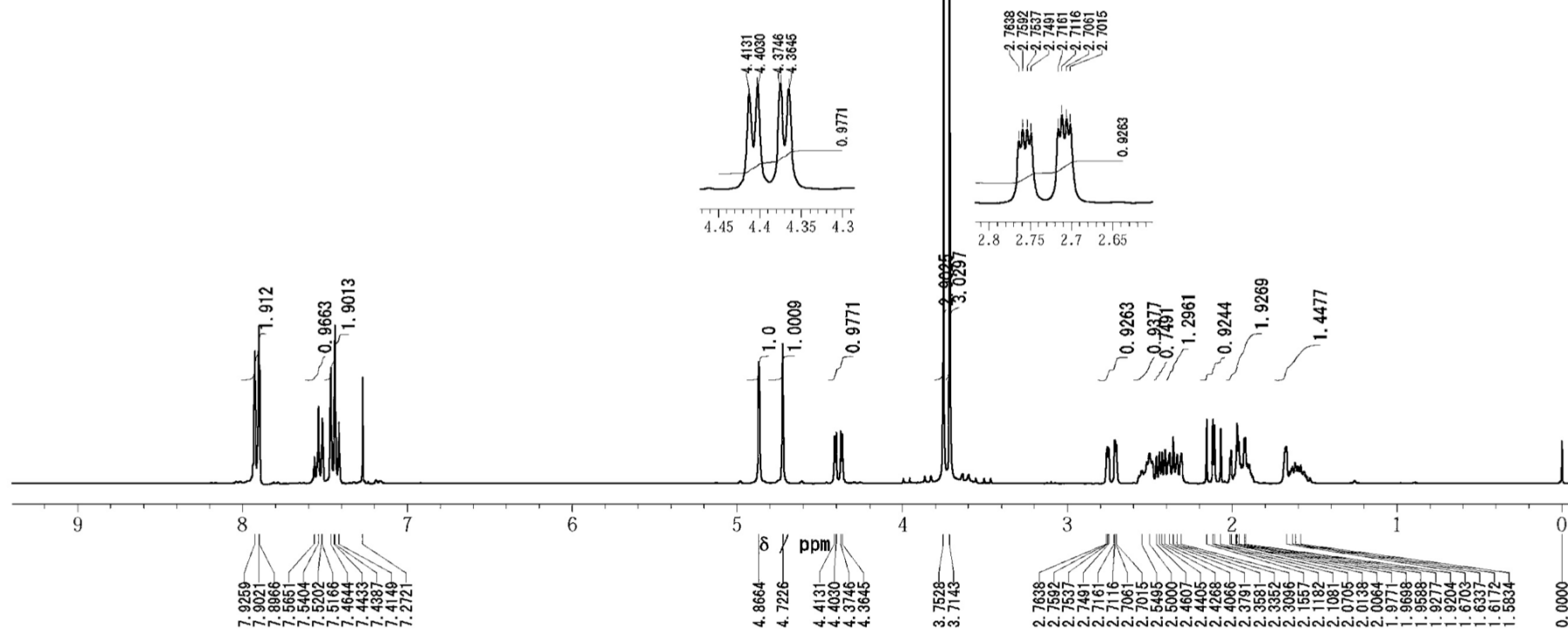
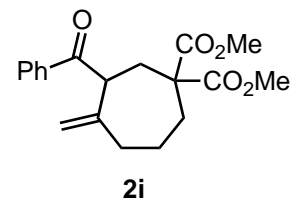


Original File:
 Date Jun 17 10
 Comment C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode N0H
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 8768
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 22:34:34
 Operator

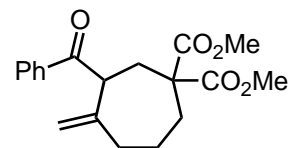


Original File: Jun 25 10
 Date: Jun 25 10
 Comment: STANDARD 1H OBSERVE
 ObsRuoc: 1H
 ExMode: NMR
 ObsFreq: 299.96 MHz
 ObsSet: -1.0 kHz
 ObsFine: 995.0047 Hz
 Point: 16384
 Frequency(Span): 4500.45 Hz
 Scan: 32
 AcqTime: 3.4983 s
 PD: 1.502 s
 Pulse1: 6.0 μ s
 Temperature: 29.0 $^{\circ}$ C
 Solvent: CDCl₃
 Reference: 0.0 ppm
 Broad.Factor: 0.1373 Hz
 RGain: 12
 Printed: 2010/Jul/30 09:33:58
 Operator:

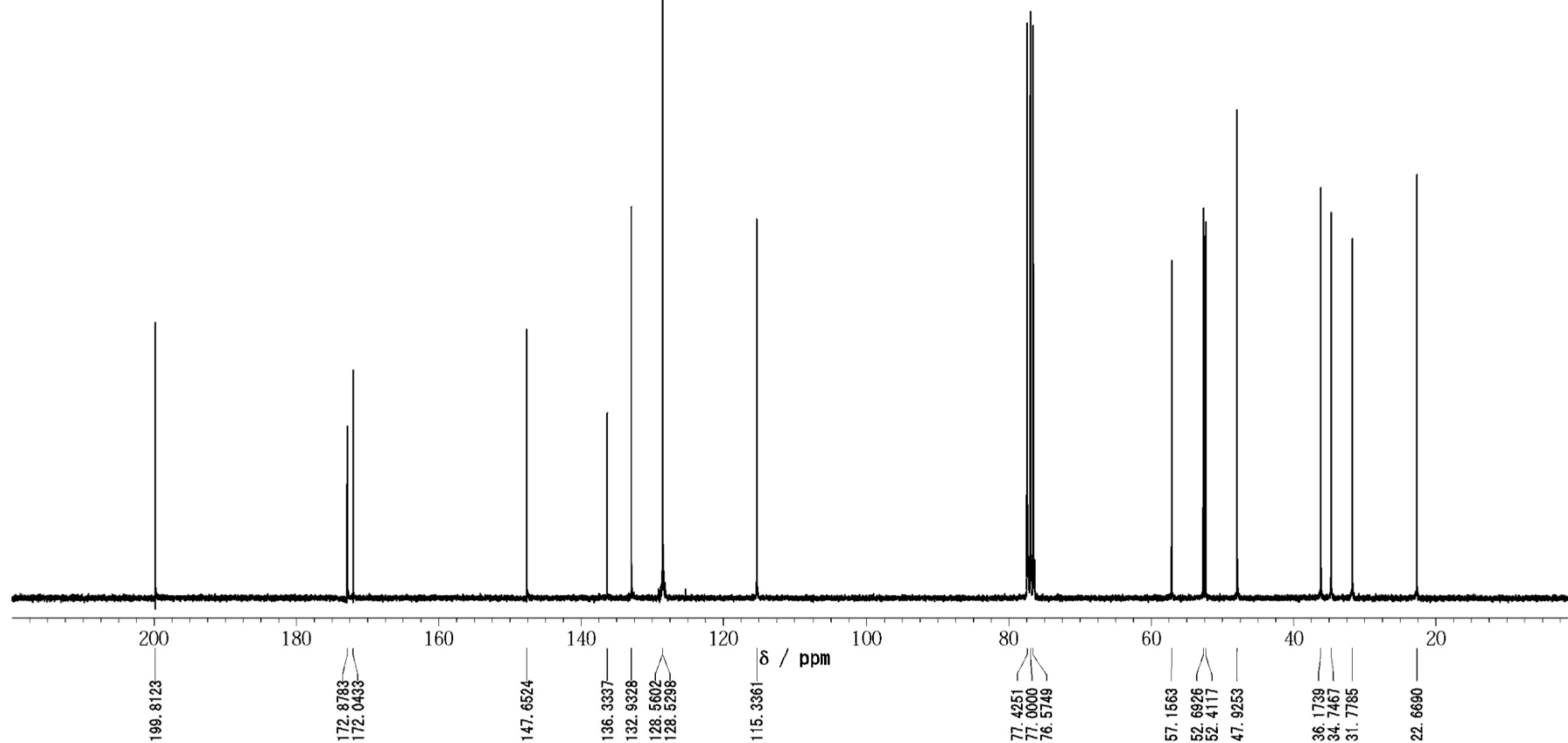


Original File:
 Date Jun 25 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

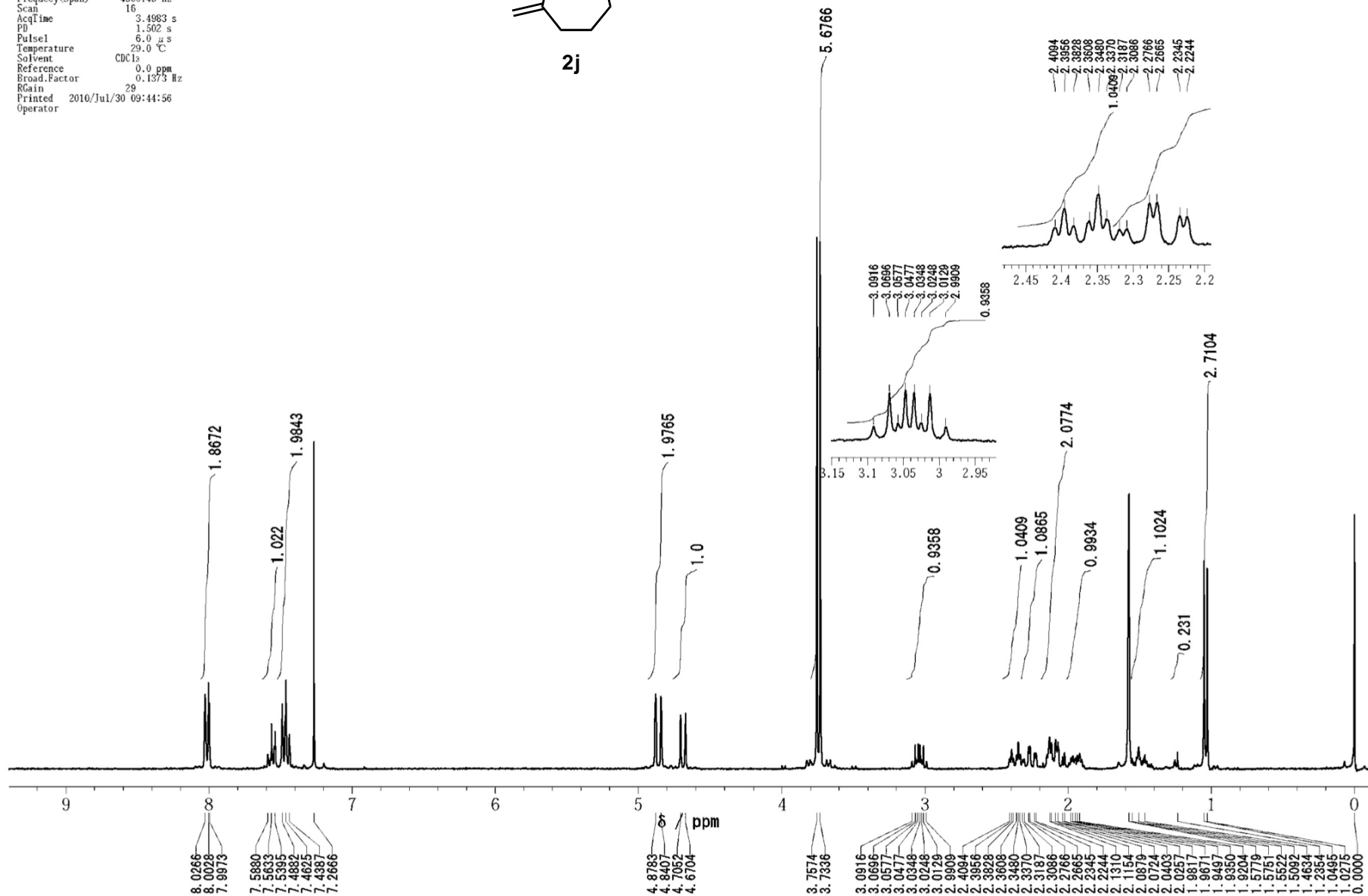
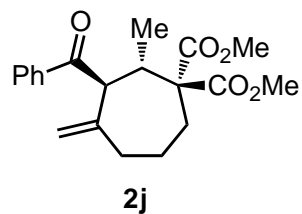
ObsRoc 13C
 ExMode N0H
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 18112
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 09:35:01
 Operator



2i

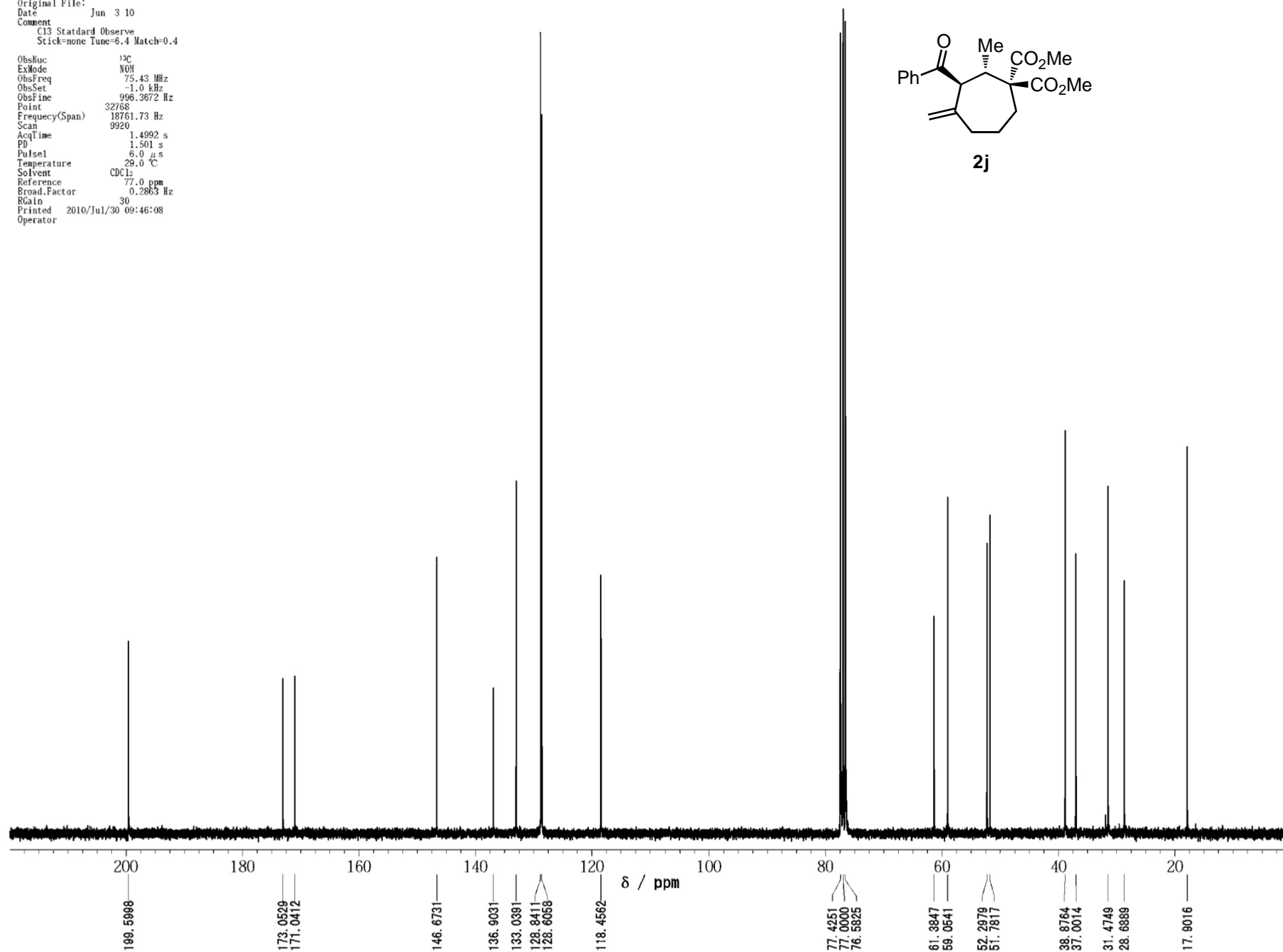
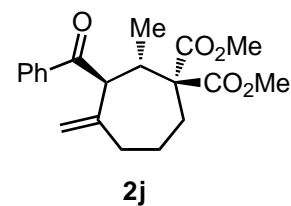


Original File: Jun 3 10
 Date: Jun 3 10
 Comment: STANDARD 1H OBSERVE
 ObsRuoc: 1H
 ExMode: NMR
 ObsFreq: 299.96 MHz
 ObsSet: -1.0 kHz
 ObsFine: 995.0047 Hz
 Point: 16384
 Frequency(Span): 4500.45 Hz
 Scan: 16
 AcqTime: 3.4983 s
 PD: 1.502 s
 Pulse1: 6.0 μ s
 Temperature: 29.0 $^{\circ}$ C
 Solvent: CDCl₃
 Reference: 0.0 ppm
 Broad.Factor: 0.1373 Hz
 RGain: 29
 Printed: 2010/Jul/30 09:44:56
 Operator:



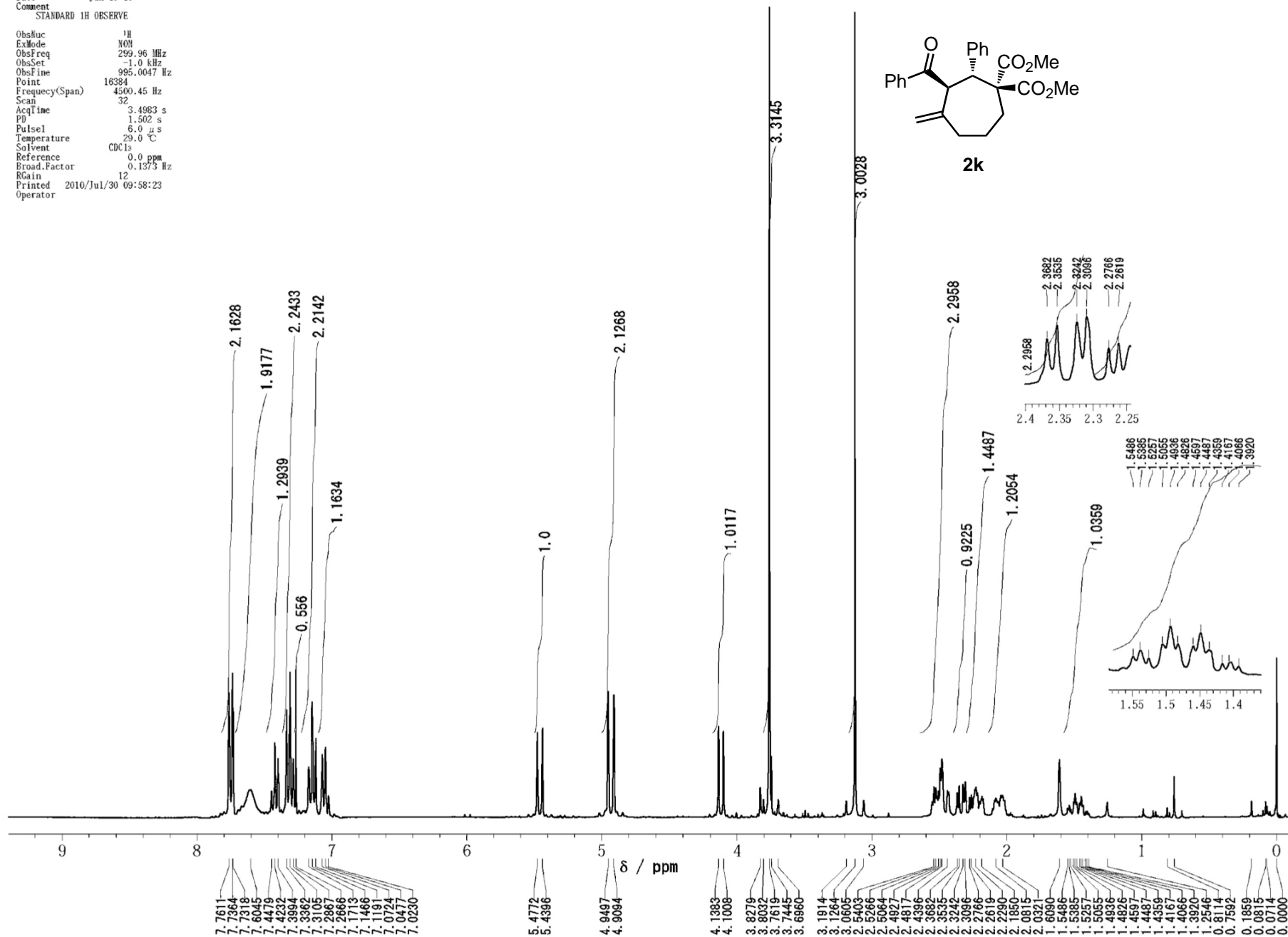
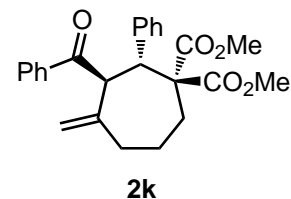
Original File: Jun 3 10
 Date
 Comment C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 9920
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 09:46:08
 Operator



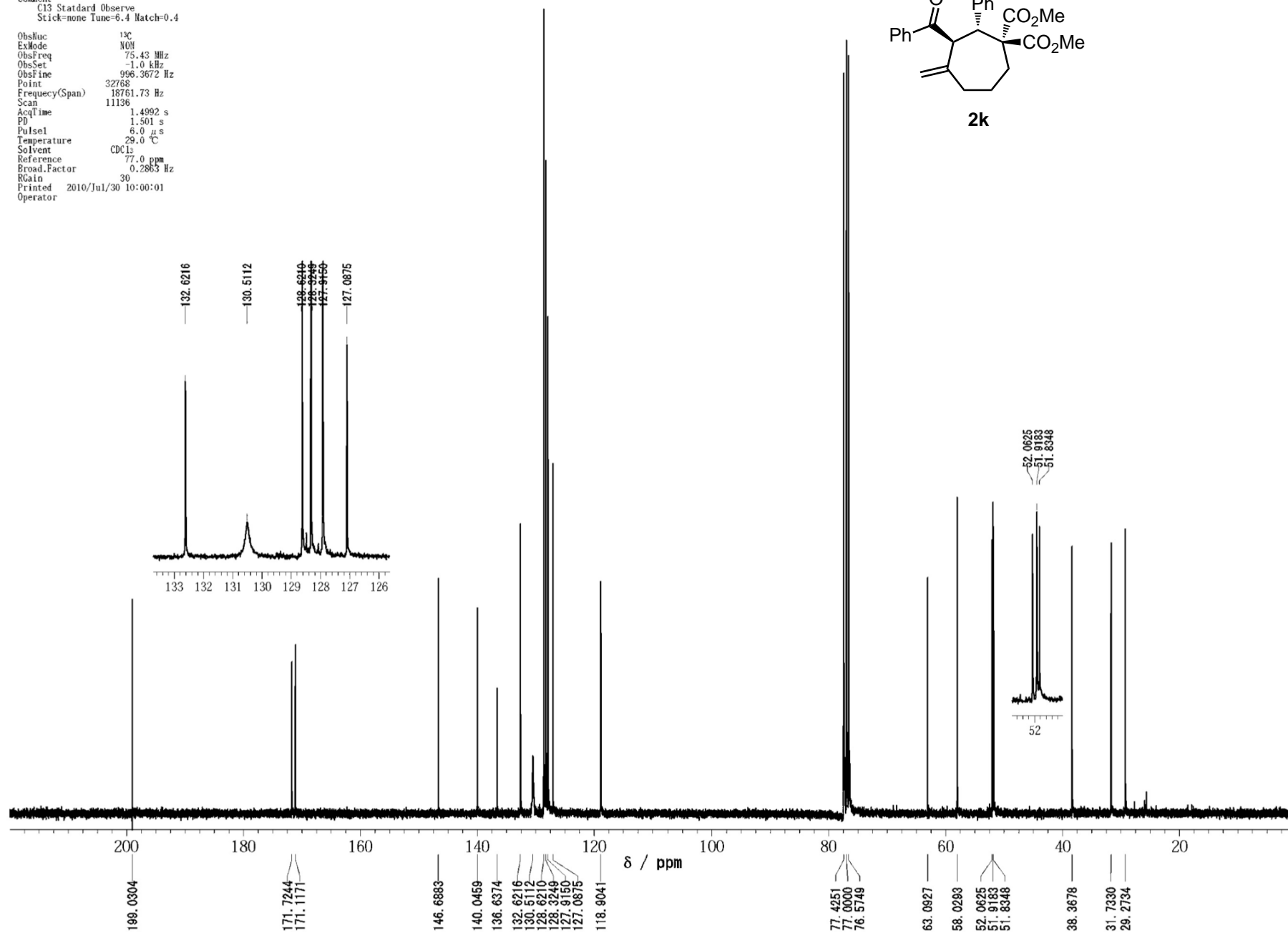
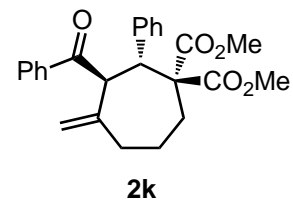
Original File:
Date Jun 15 10
Comment
STANDARD 1H OBSERVE

ObsRuac 1H
ExMode N08
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 12
Printed 2010/Jul/30 09:58:23
Operator



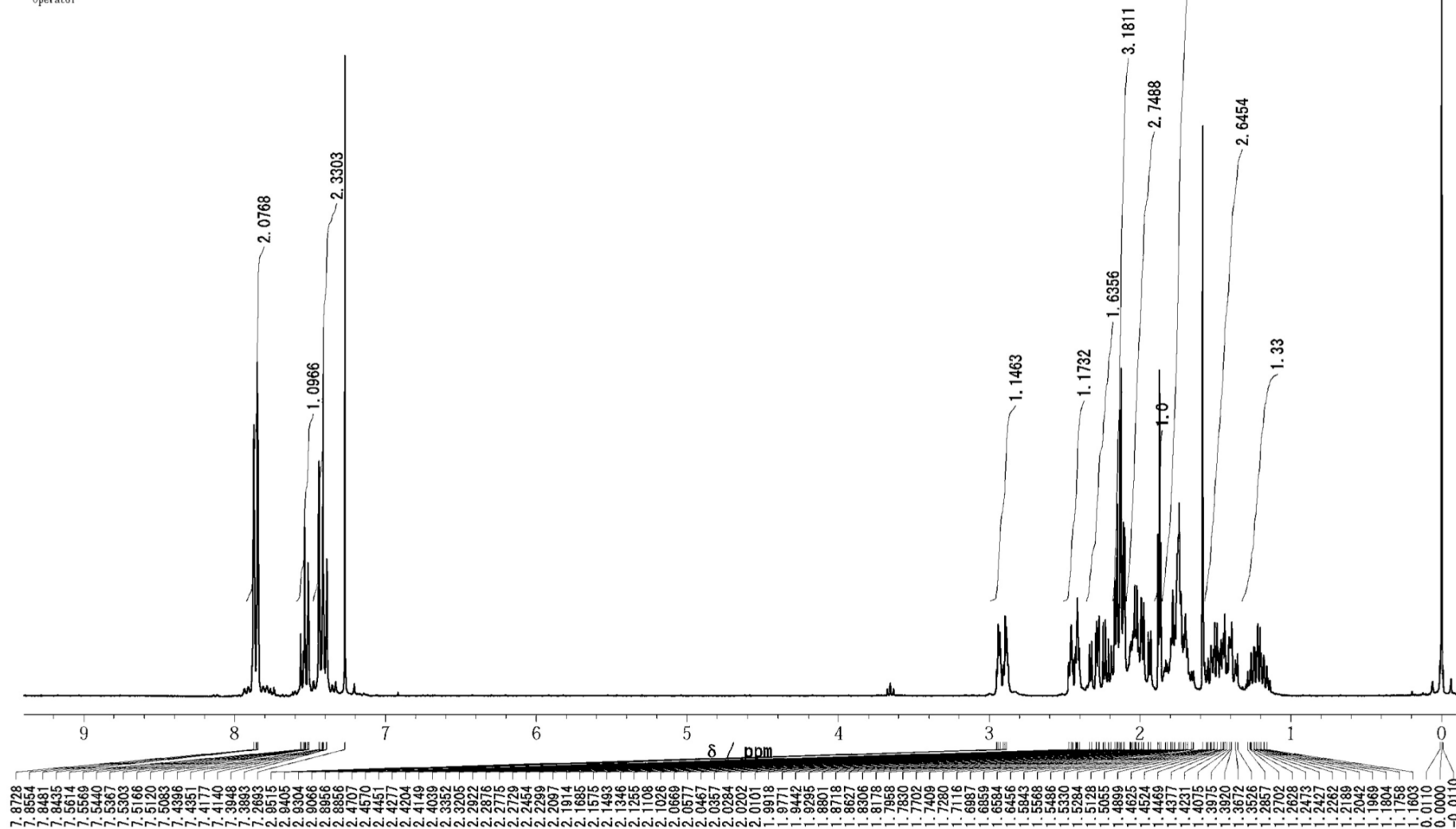
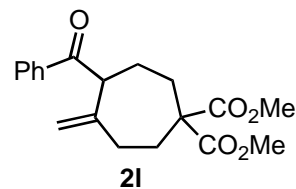
Original File:
 Date Jun 15 10
 Comment C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 11136
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 10:00:01
 Operator



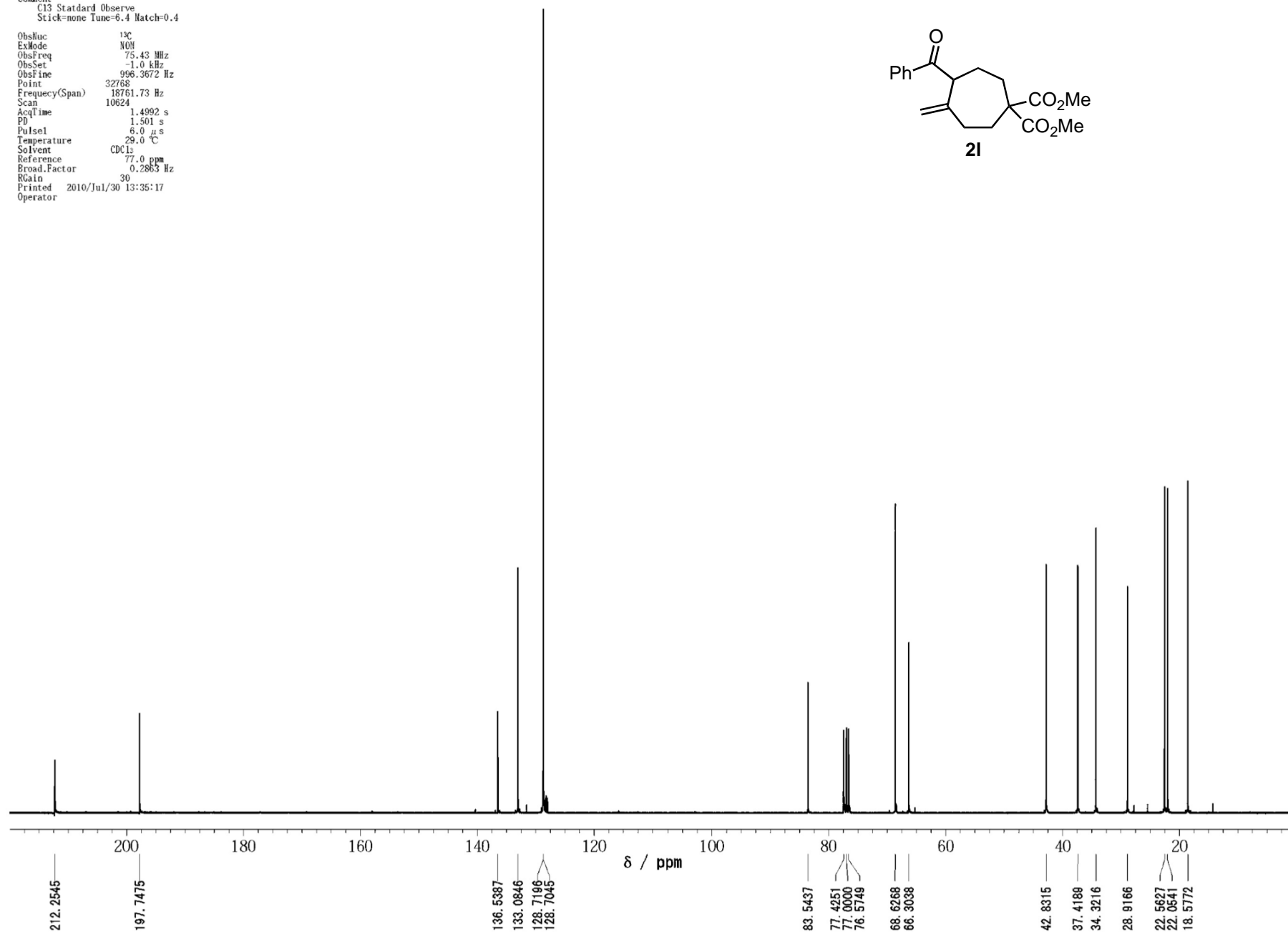
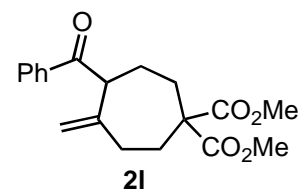
Original File:
Date Jun 15 10
Comment
STANDARD 1H OBSERVE

ObsMod ¹H
ExMode NOE
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 96
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 19
Printed 2010/Jul/30 13:33:19
Operator



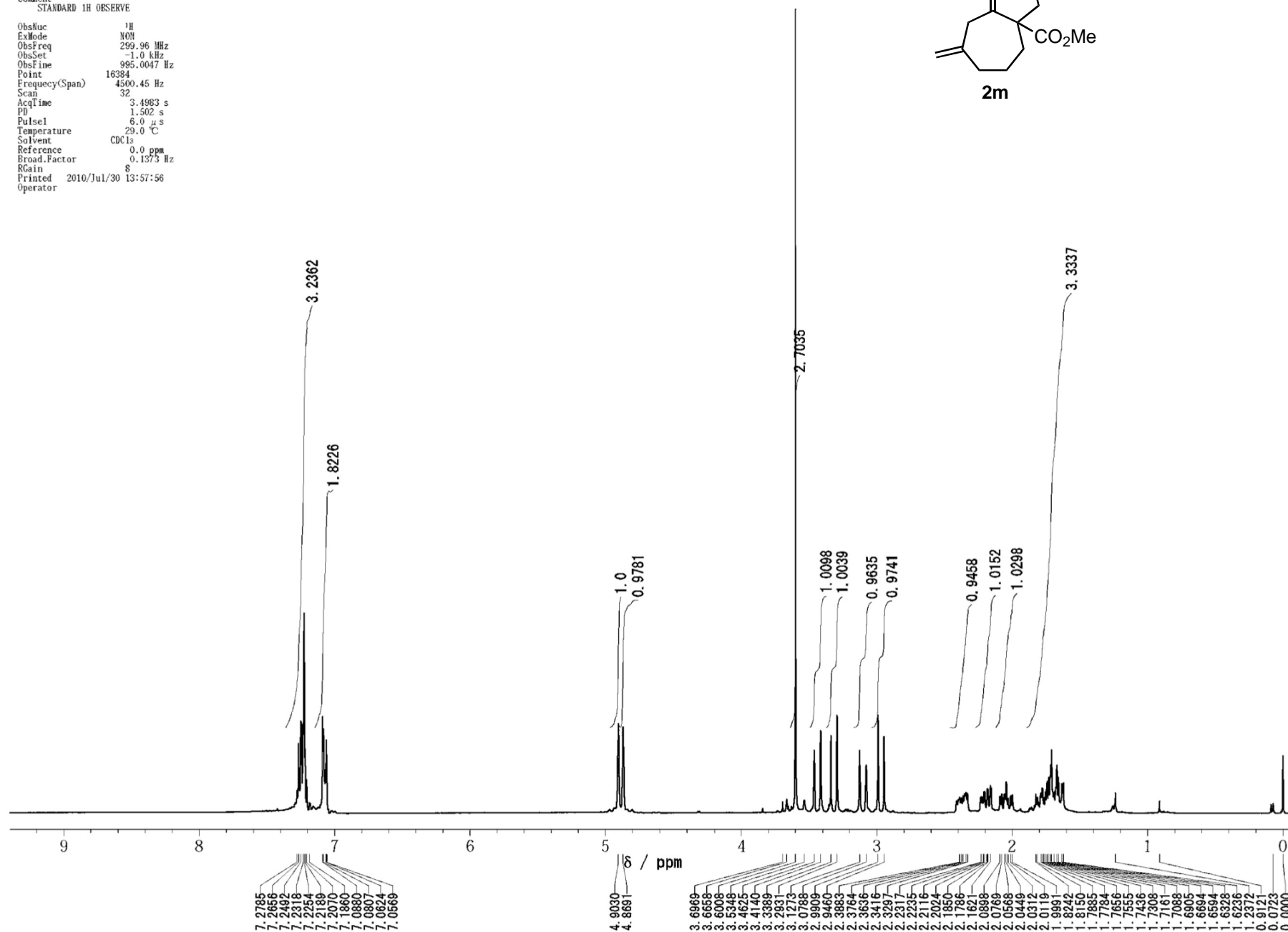
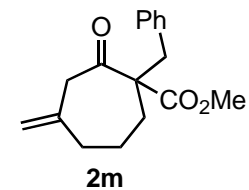
Original File:
 Date Jun 15 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 10624
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 13:35:17
 Operator



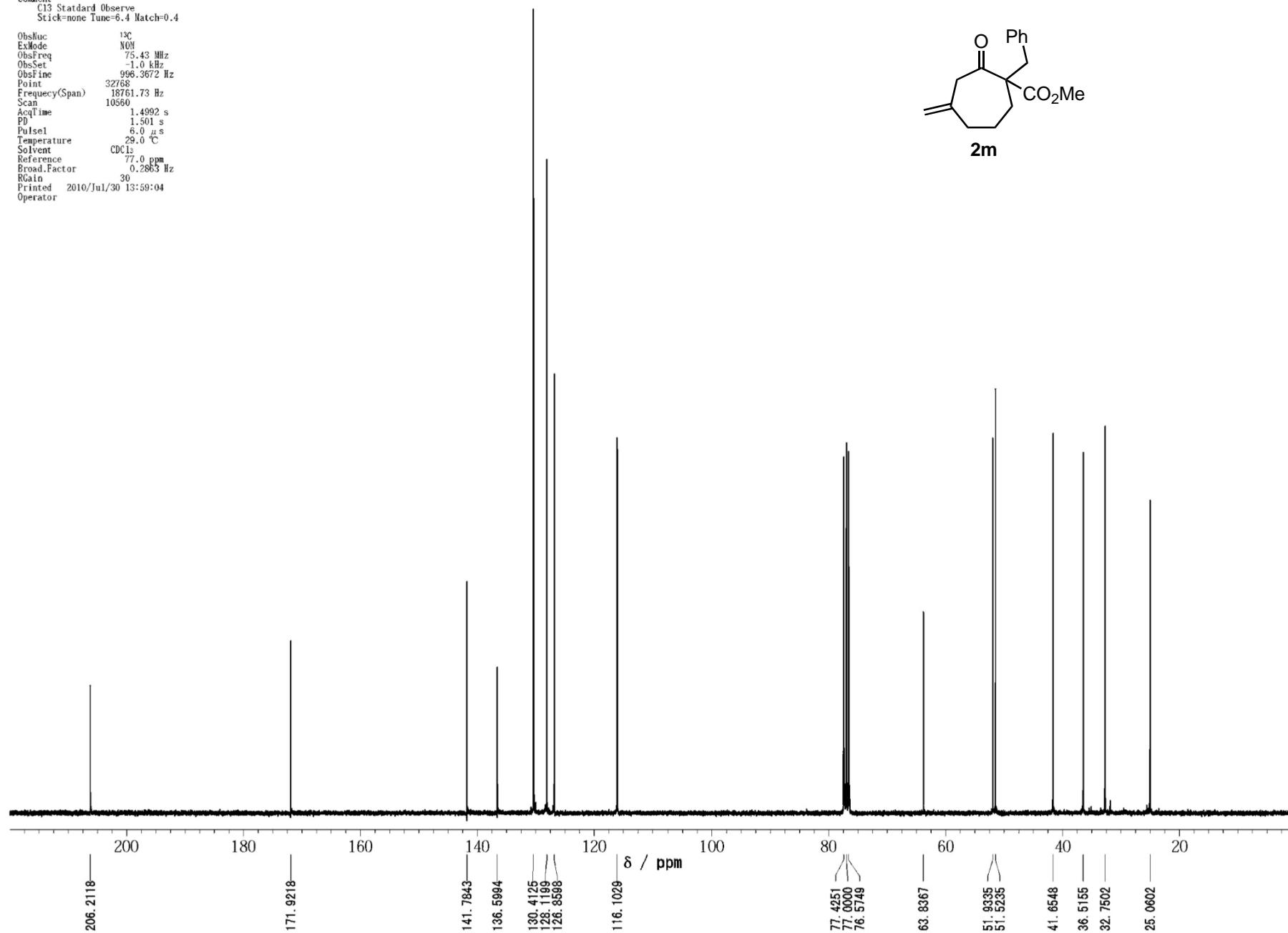
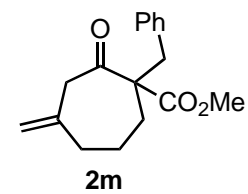
Original File:
Date May 28 10
Comment
STANDARD 1H OBSERVE

ObsRuoc ¹H
ExMode NMR
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 32
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 8
Printed 2010/Jul/30 13:57:56
Operator

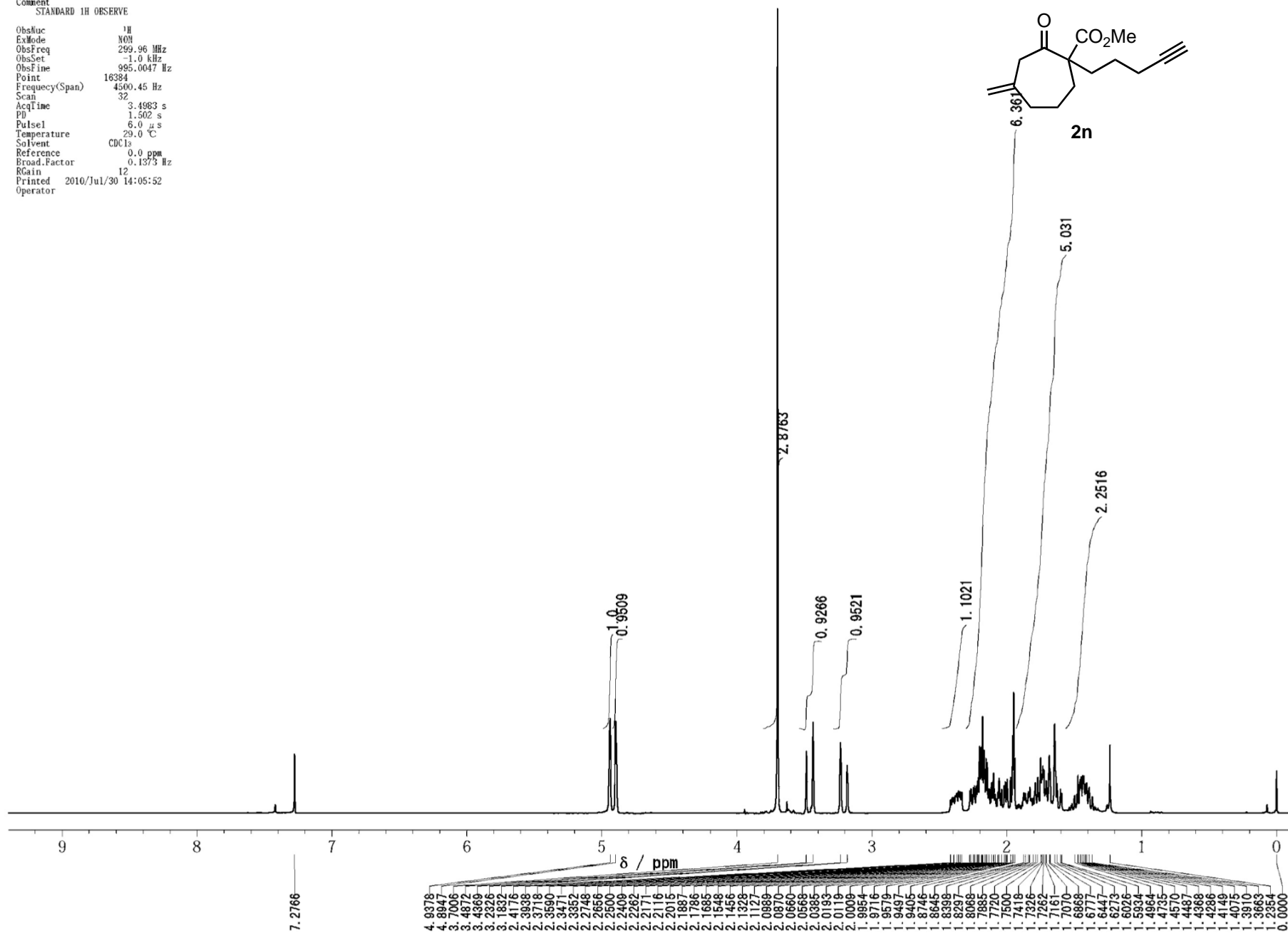


Original File:
 Date May 28 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 10560
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 13:59:04
 Operator



Original File: Jun 25 10
 Date
 Comment
 STANDARD 1H OBSERVE
 ObsRuoc ¹H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 12
 Printed 2010/Jul/30 14:05:52
 Operator

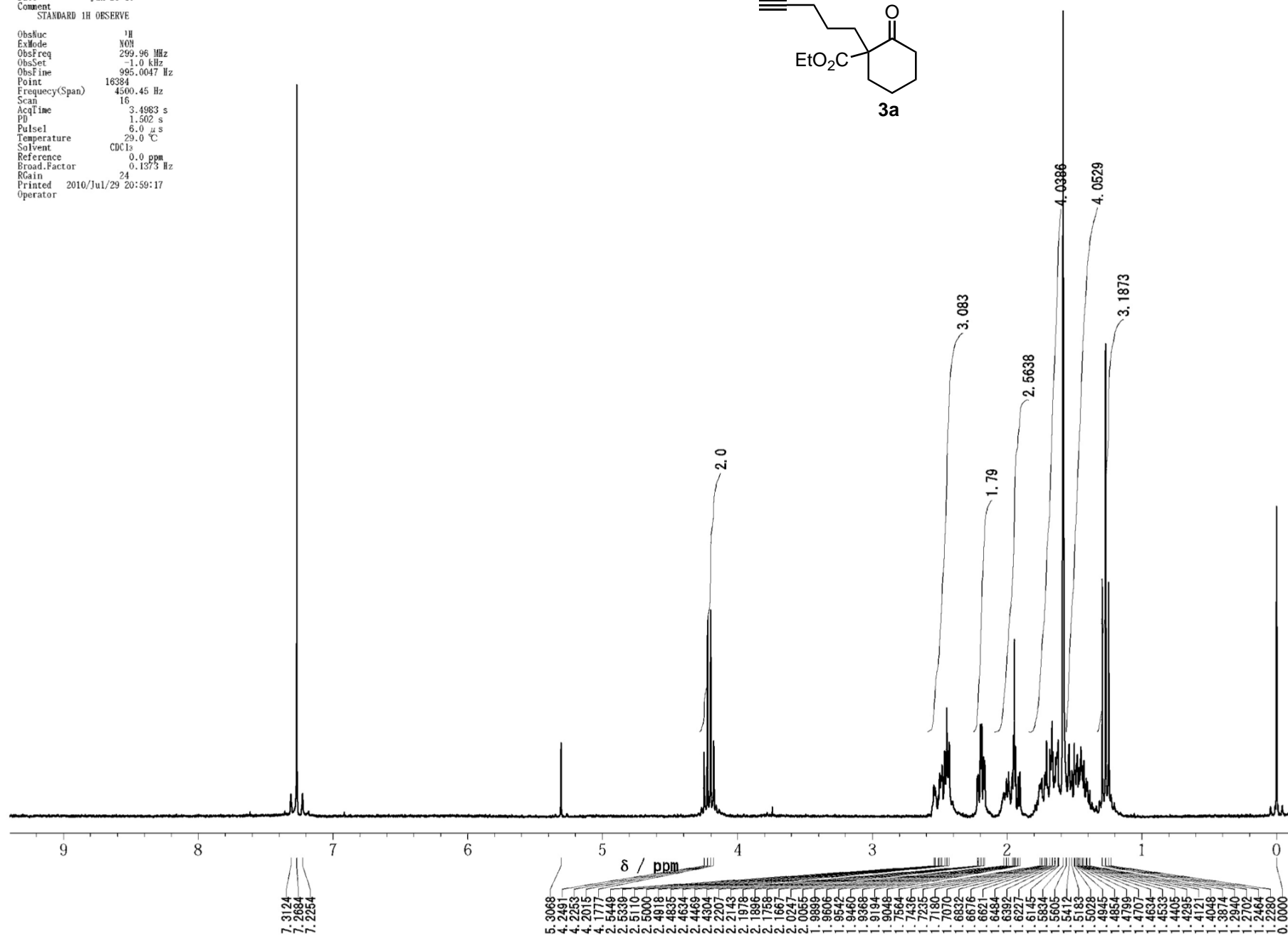
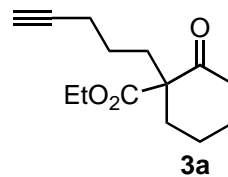


ObsSfuc	13C
ExMode	NON
ObsFreq	75.43 MHz
ObsSet	-1.0 kHz
ObsLine	996.3672 Hz
Point	32768
Frequency(Span)	18761.73 Hz
Scan	9984
AcqTime	1.4992 s
PD	1.501 s
Pulse1	6.0 μ s
Temperature	29.0 $^{\circ}$ C
Solvent	CDCl ₃
Reference	77.0 ppm
Broad.Factor	0.2863 Hz
RGain	30
Printed	2010/Jul/30 14:07:39
Operator	

C#CCCC1(C(=O)OC)CCCCC1=C

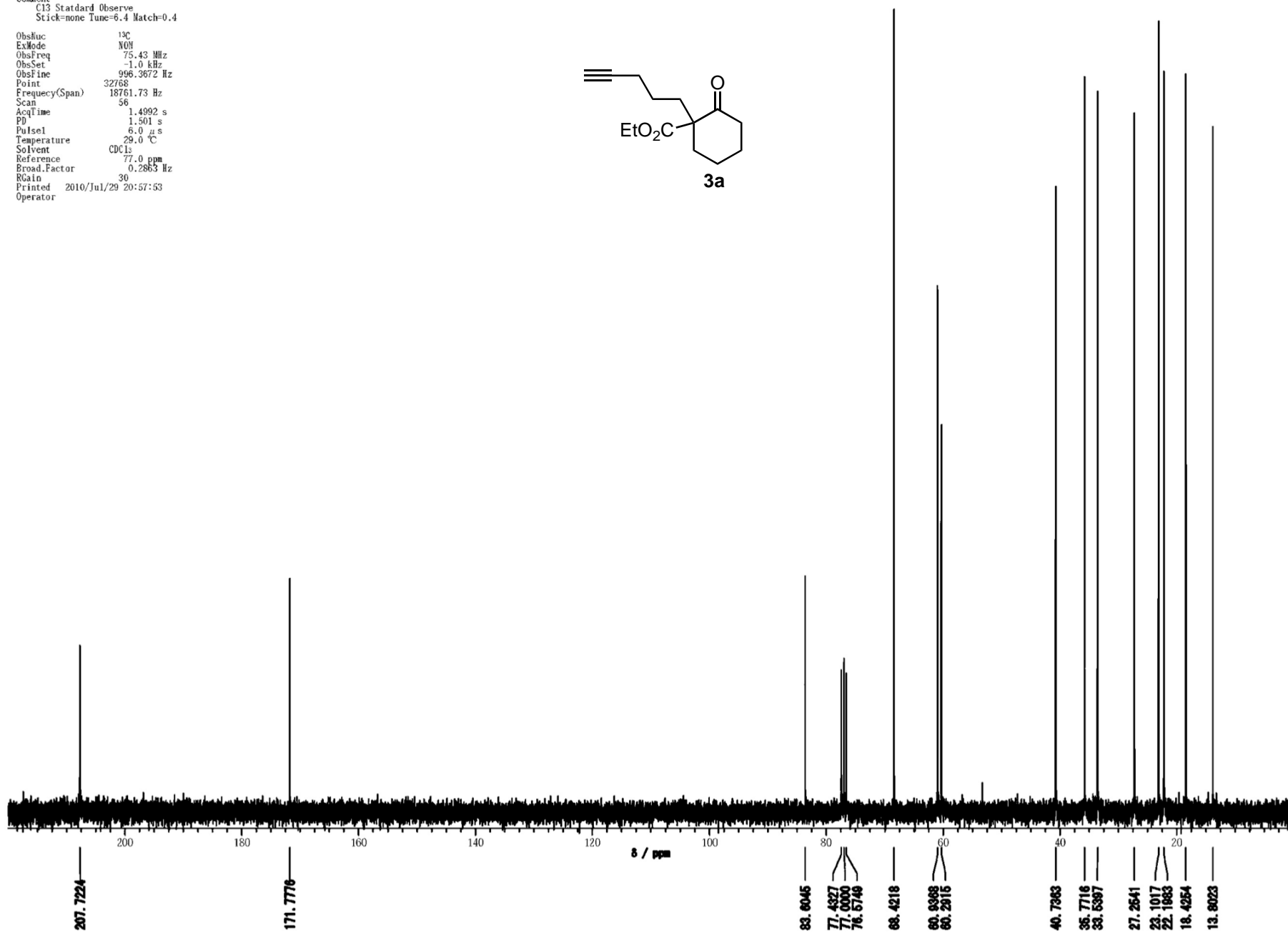
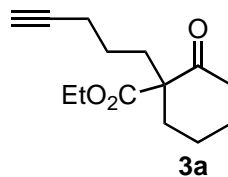
2n

Original File: Jun 28 10
 Date
 Comment
 STANDARD 1H OBSERVE
 ObsRuoc ¹H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 16
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/29 20:59:17
 Operator



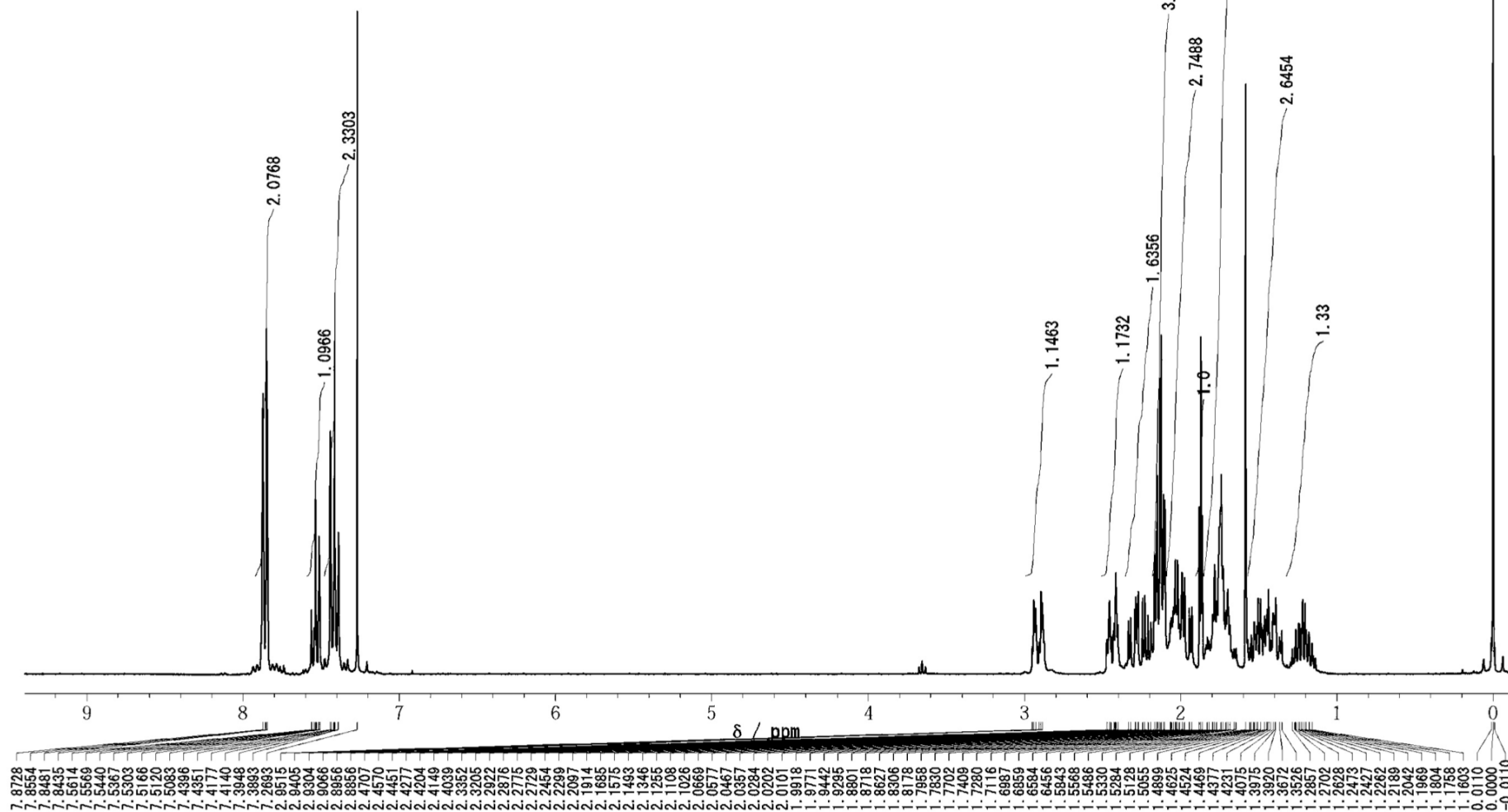
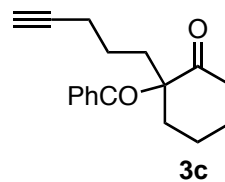
Original File:
 Date Jun 28 10
 Comment
 C13 Statdard Observe
 Stick=none Tune=6.4 Match=0.4

Obskuc ¹³C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 56
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μs
 Temperature 29.0 °C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 20:57:53
 Operator



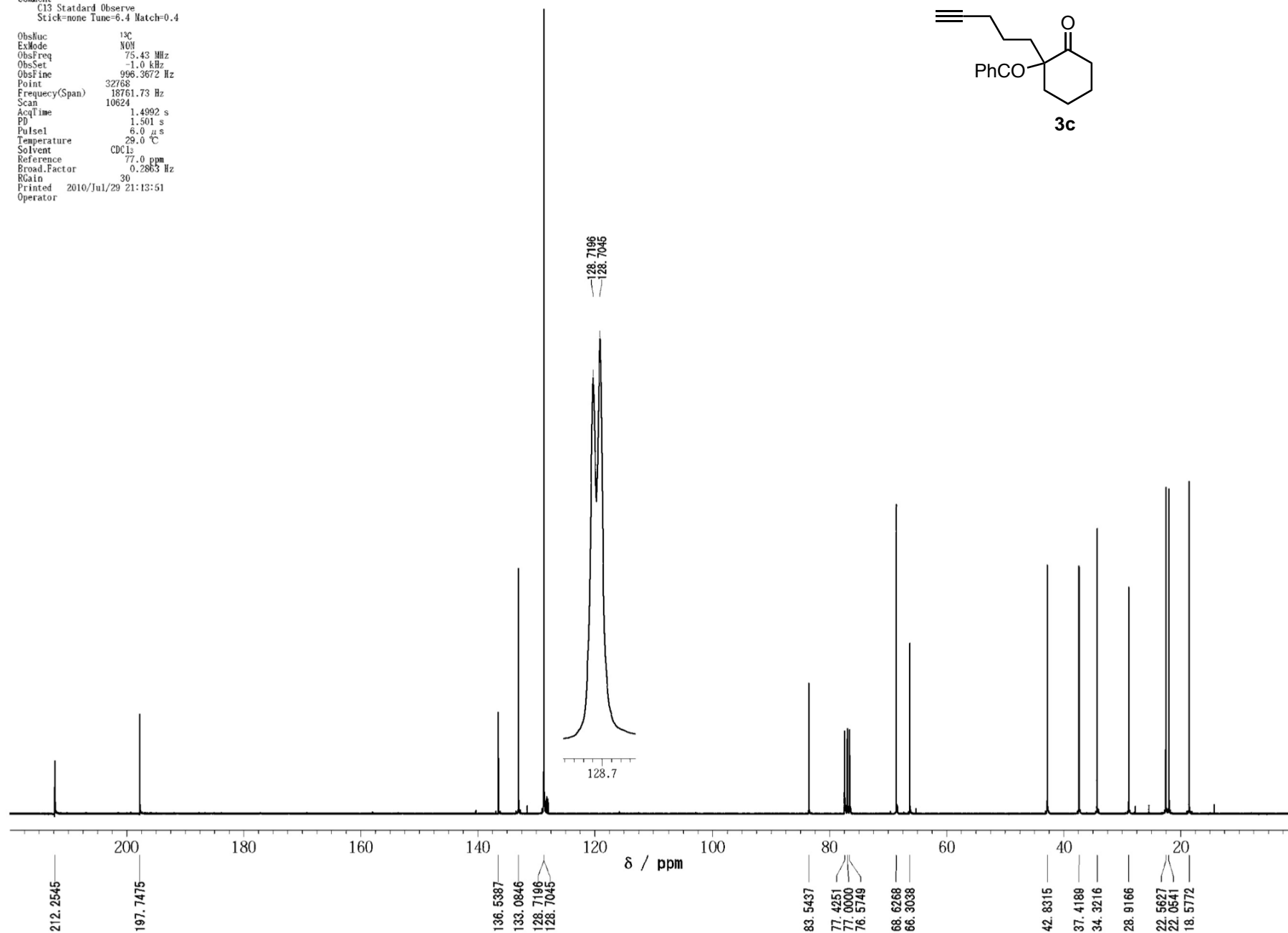
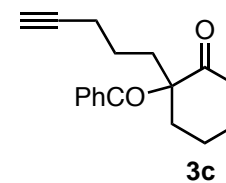
Original File:
Date Jun 15 10
Comment
STANDARD 1H OBSERVE

ObsRuoc 1H
ExMode NMR
ObsFreq 299.96 MHz
ObsSet -1.0 kHz
ObsFine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 96
AcqTime 3.4983 s
PD 1.502 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad.Factor 0.1373 Hz
RGain 19
Printed 2010/Jul/29 21:11:36
Operator

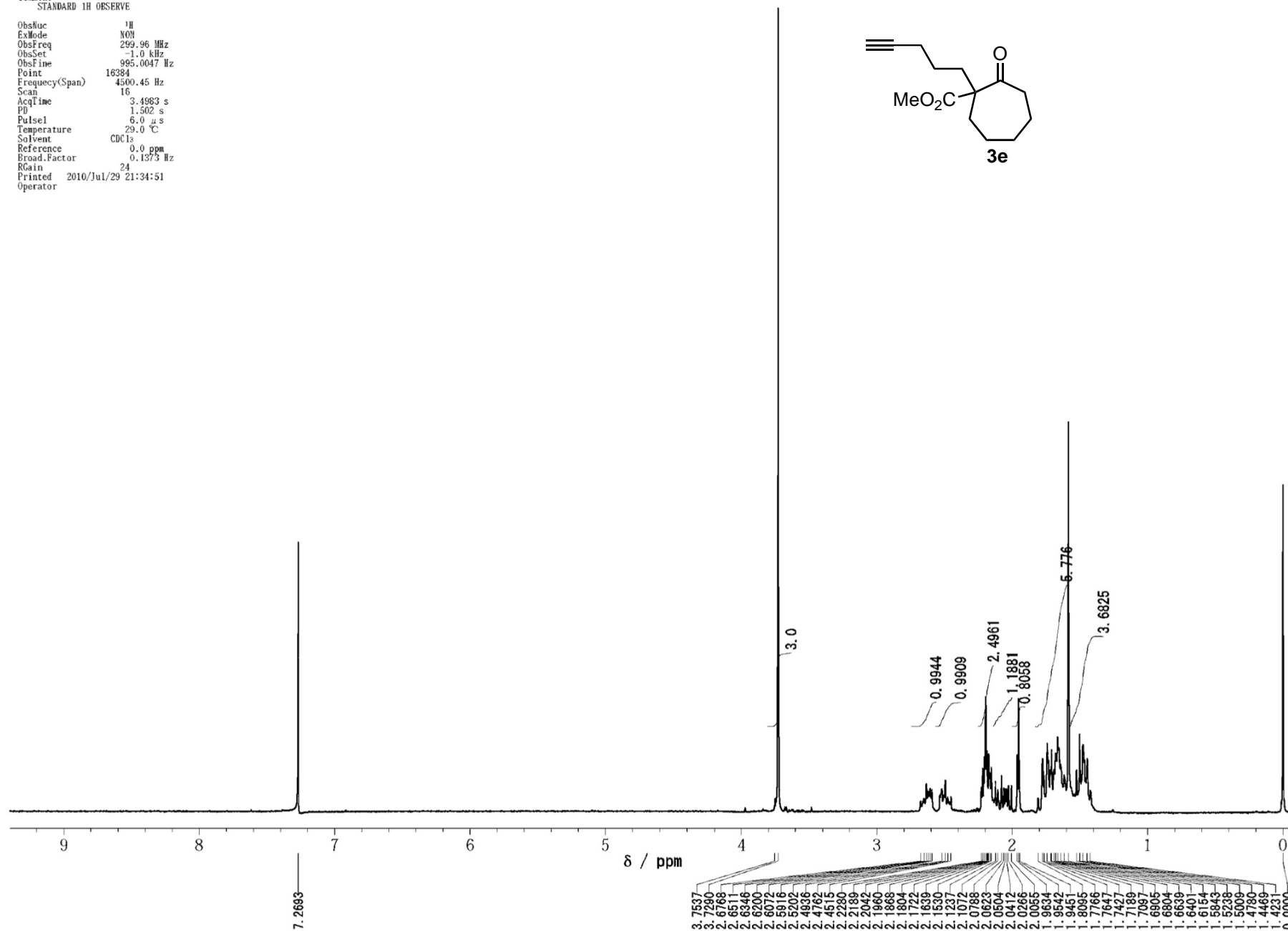
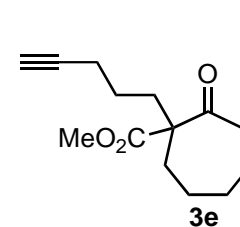


Original File:
 Date Jun 15 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 10624
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 21:13:51
 Operator

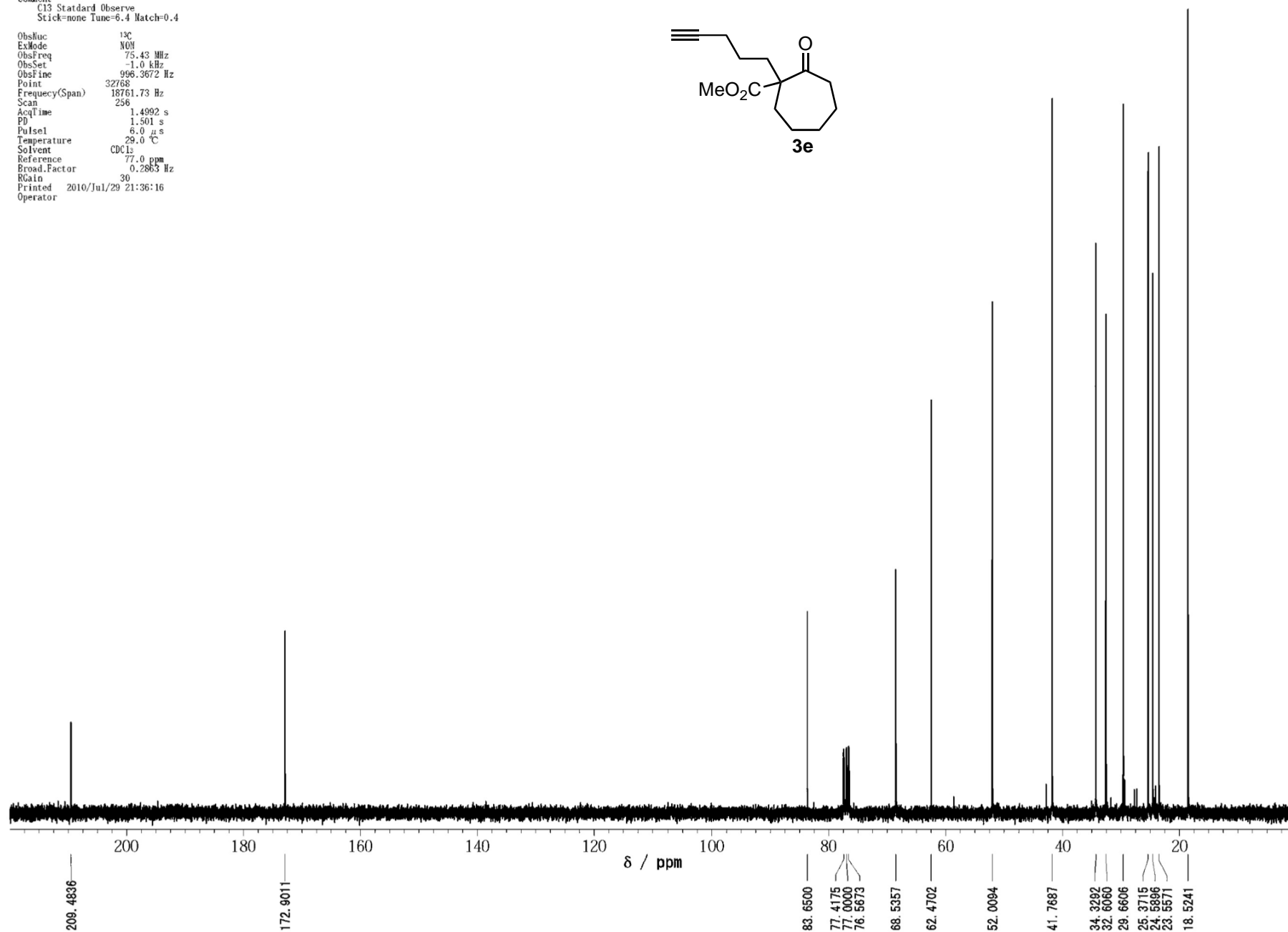
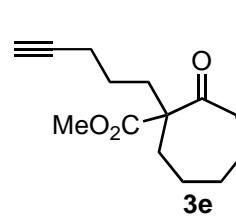


Original File: Oct 2 09
 Date
 Comment
 STANDARD 1H OBSERVE
 ObsRuoc 1H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 16
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/29 21:34:51
 Operator

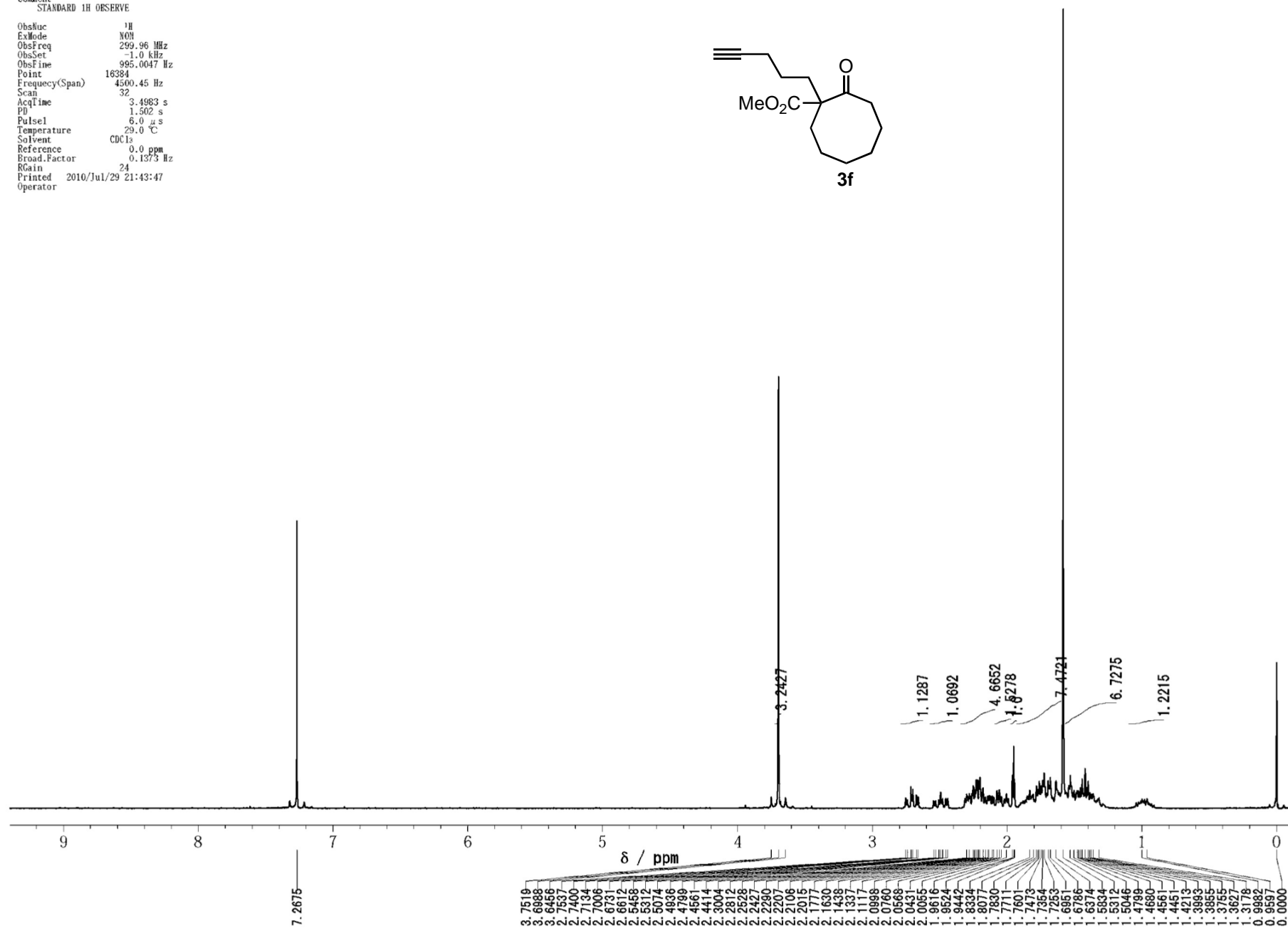
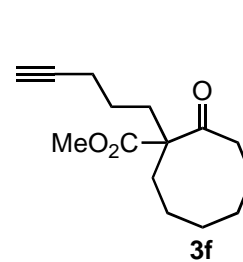


Original File:
 Date Oct 2 09
 Comment C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 256
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 21:36:16
 Operator

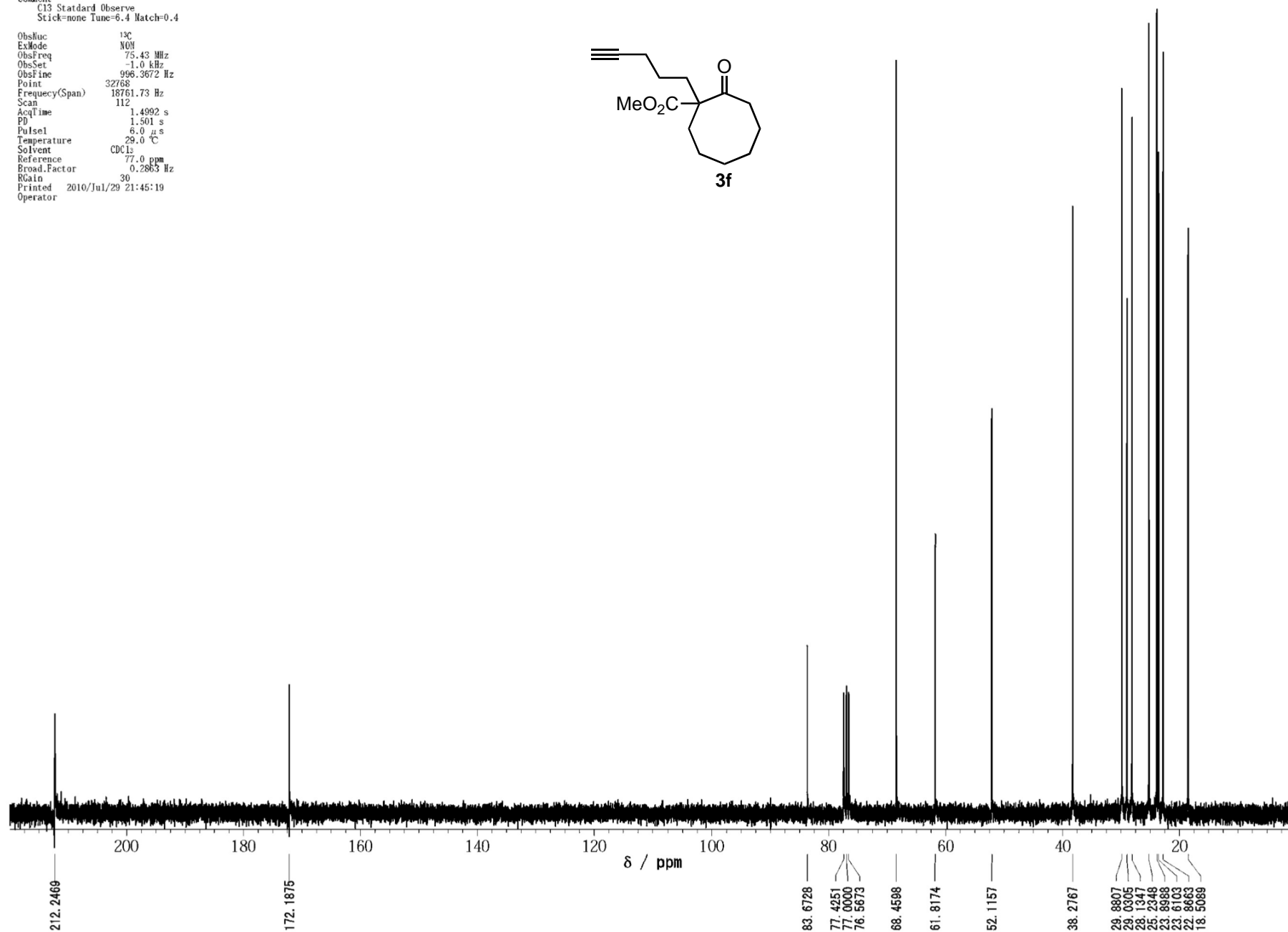
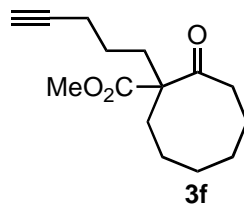


Original File:
 Date Jul 23 10
 Comment
 STANDARD 1H OBSERVE
 ObsRuoc ¹H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/29 21:43:47
 Operator



Original File:
 Date Jul 23 10
 Comment C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 112
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 21:45:19
 Operator



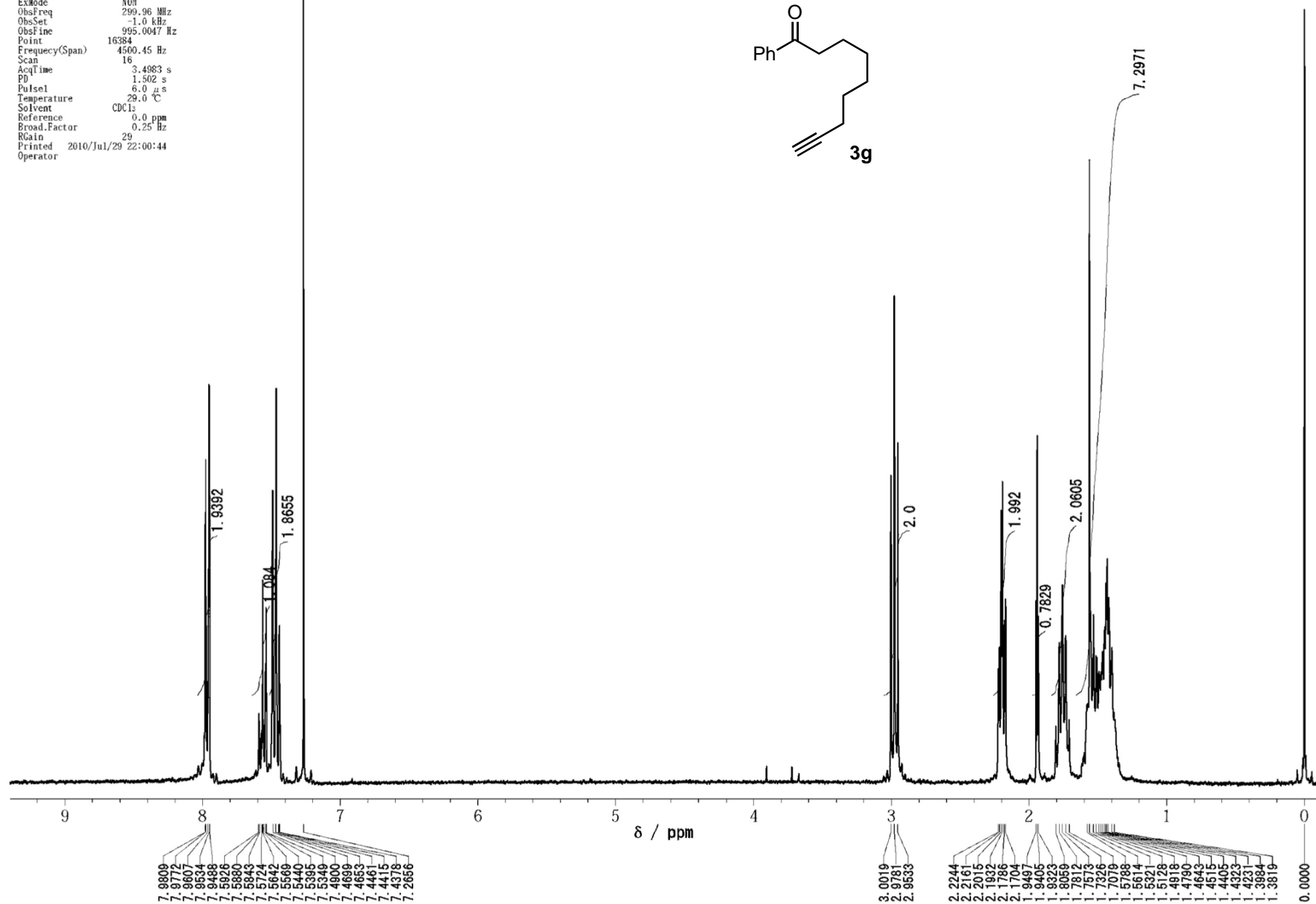
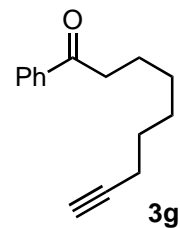
Original File: C:\DOCUMENTS AND SETTINGS\北海道大学\MY DOCUMENTS\DELL NMR データ 06Q14\H1DET04H1D-11-22A-FR1-1H.F

Date Feb 25 10

Comment

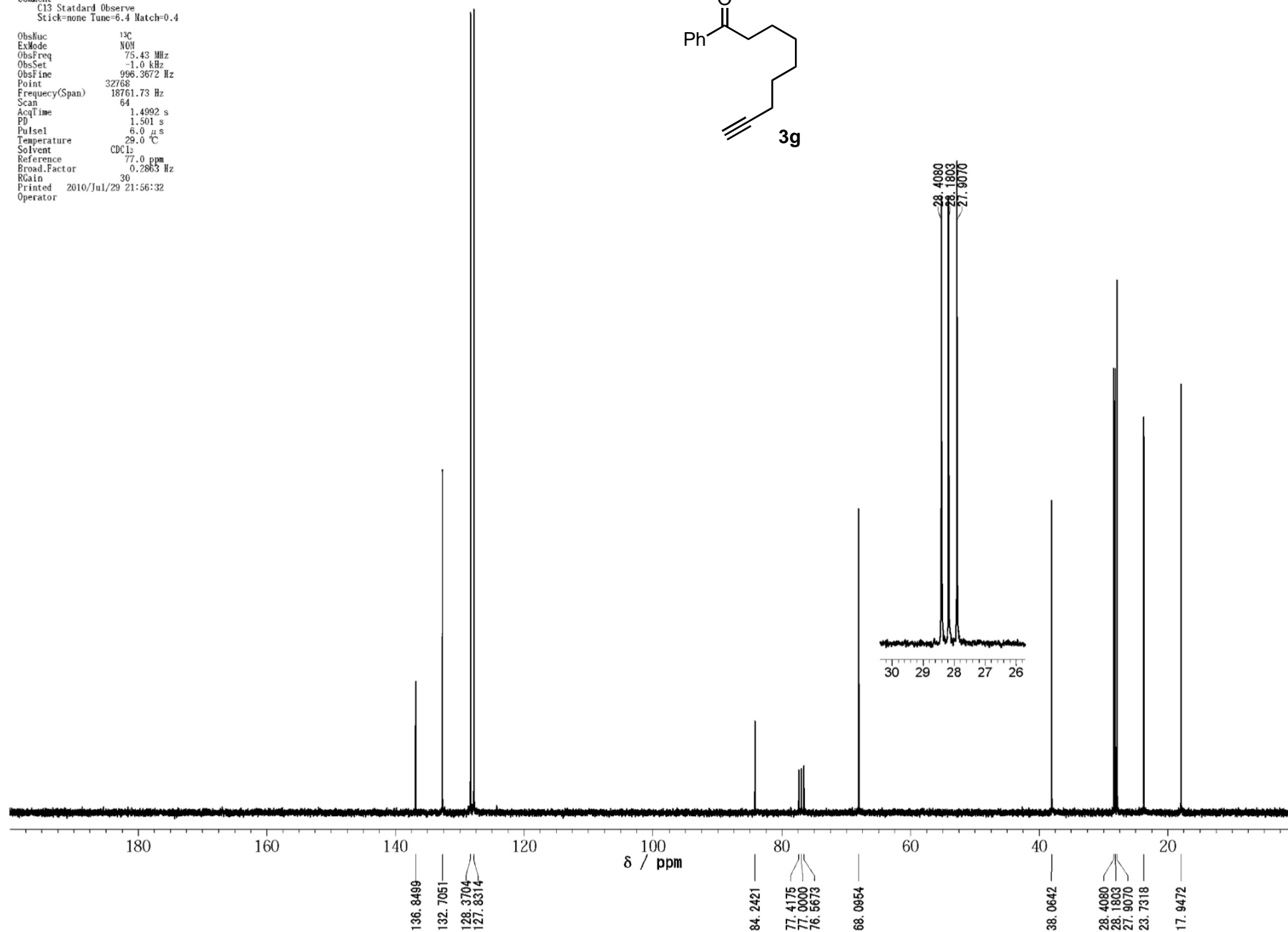
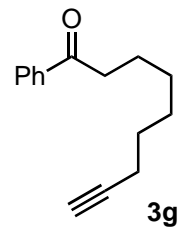
STANDARD 1H OBSERVE

Obs Nuc ¹H
Ex Mode NOE
Obs Freq 299.96 MHz
Obs Set -1.0 kHz
Obs Fine 995.0047 Hz
Point 16384
Frequency(Span) 4500.45 Hz
Scan 16
Acq Time 3.4983 s
PD 1.502 s
Pulse 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 0.0 ppm
Broad Factor 0.25 Hz
RGain 29
Printed 2010/Jul/29 22:00:44
Operator

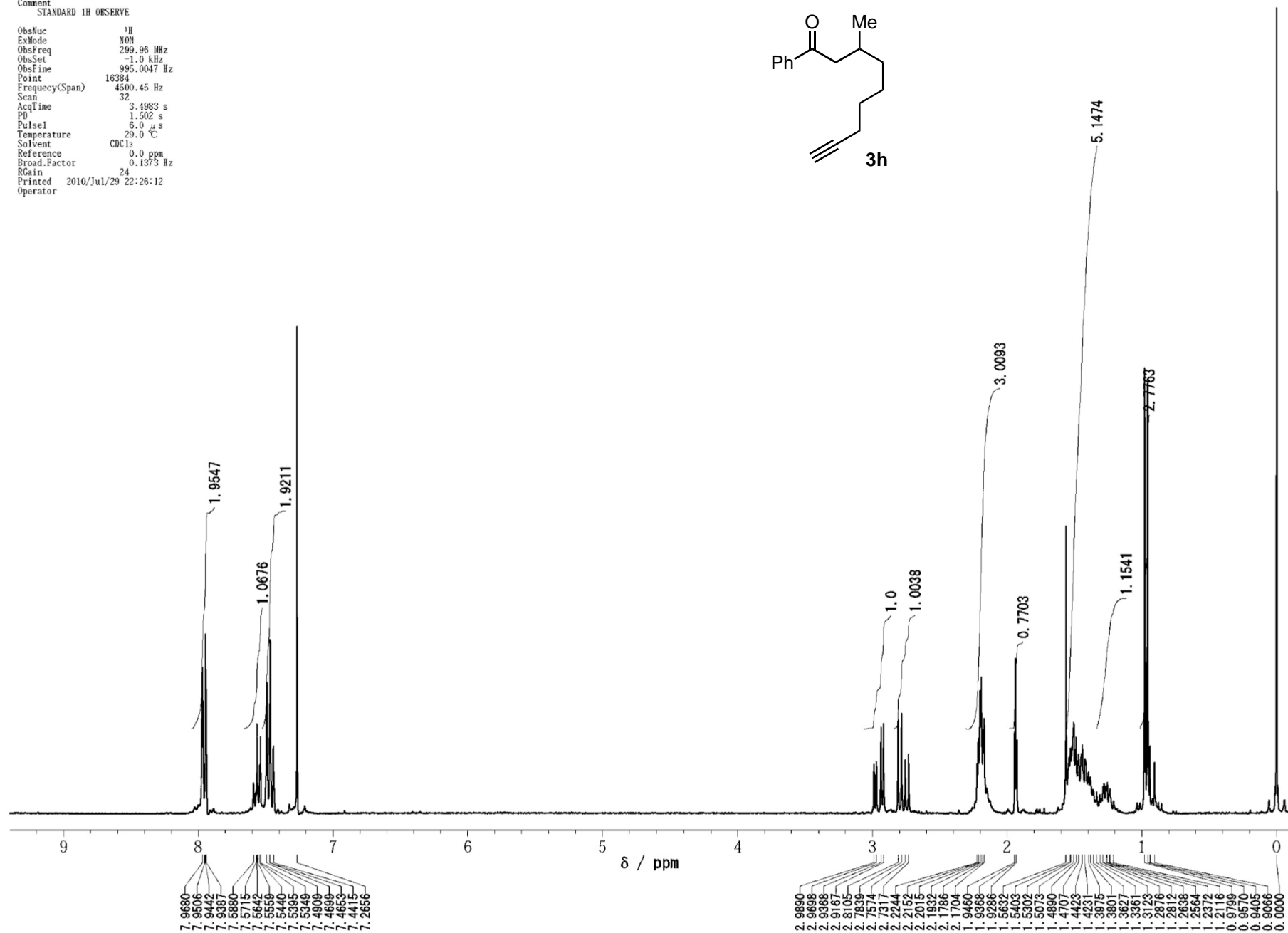
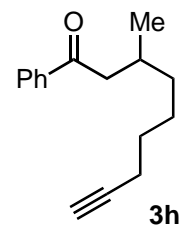


Original File:
 Date Feb 25 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 64
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 21:56:32
 Operator

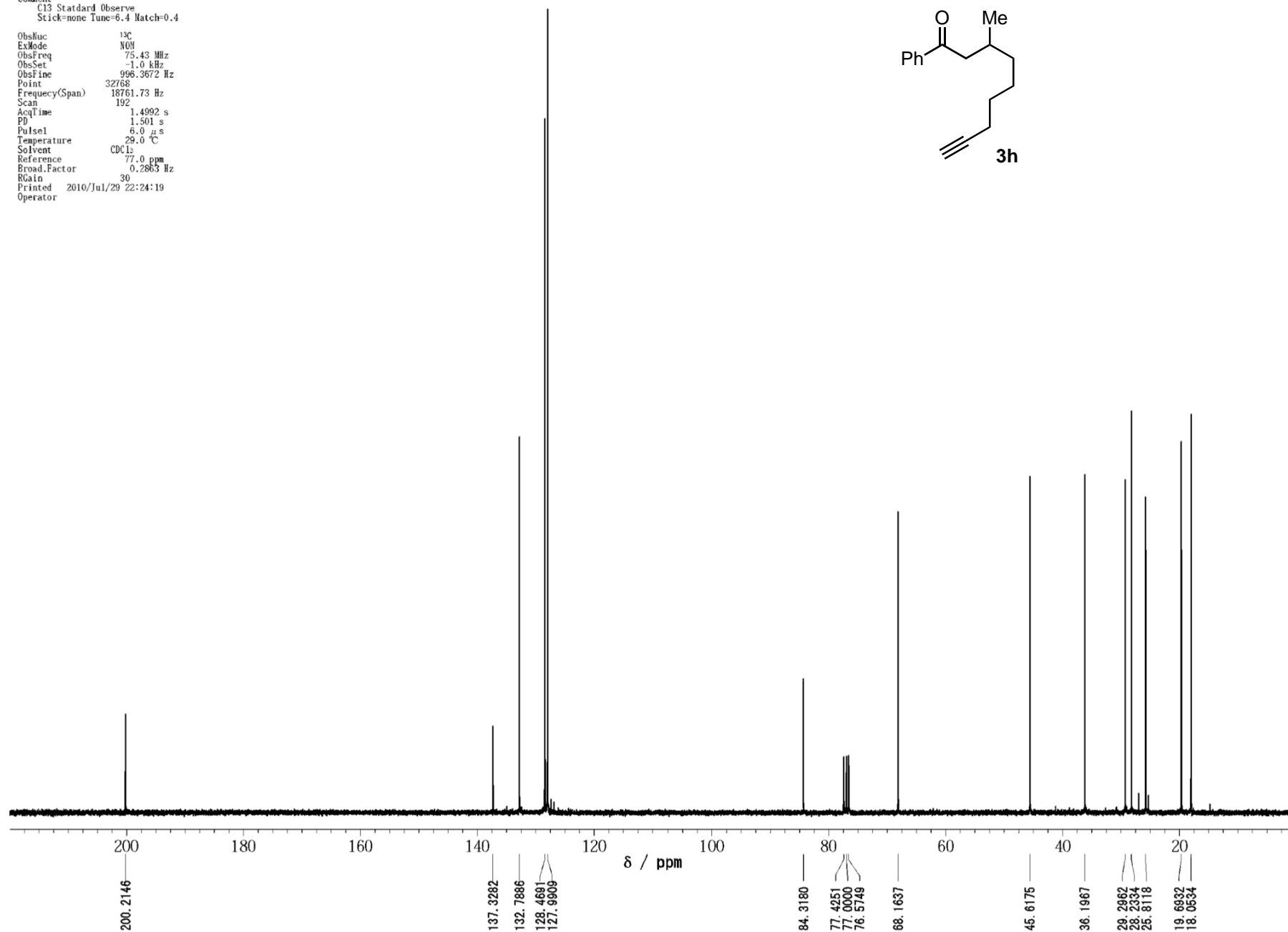
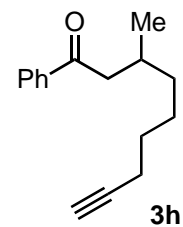


Original File: Jun 9 10
 Date: Jun 9 10
 Comment: STANDARD 1H OBSERVE
 ObsRuoc: 1H
 ExMode: NMR
 ObsFreq: 299.96 MHz
 ObsSet: -1.0 kHz
 ObsFine: 995.0047 Hz
 Point: 16384
 Frequency(Span): 4500.45 Hz
 Scan: 32
 AcqTime: 3.4983 s
 PD: 1.502 s
 Pulse1: 6.0 μ s
 Temperature: 29.0 $^{\circ}$ C
 Solvent: CDCl₃
 Reference: 0.0 ppm
 Broad.Factor: 0.1373 Hz
 RGain: 24
 Printed: 2010/Jul/29 22:26:12
 Operator:

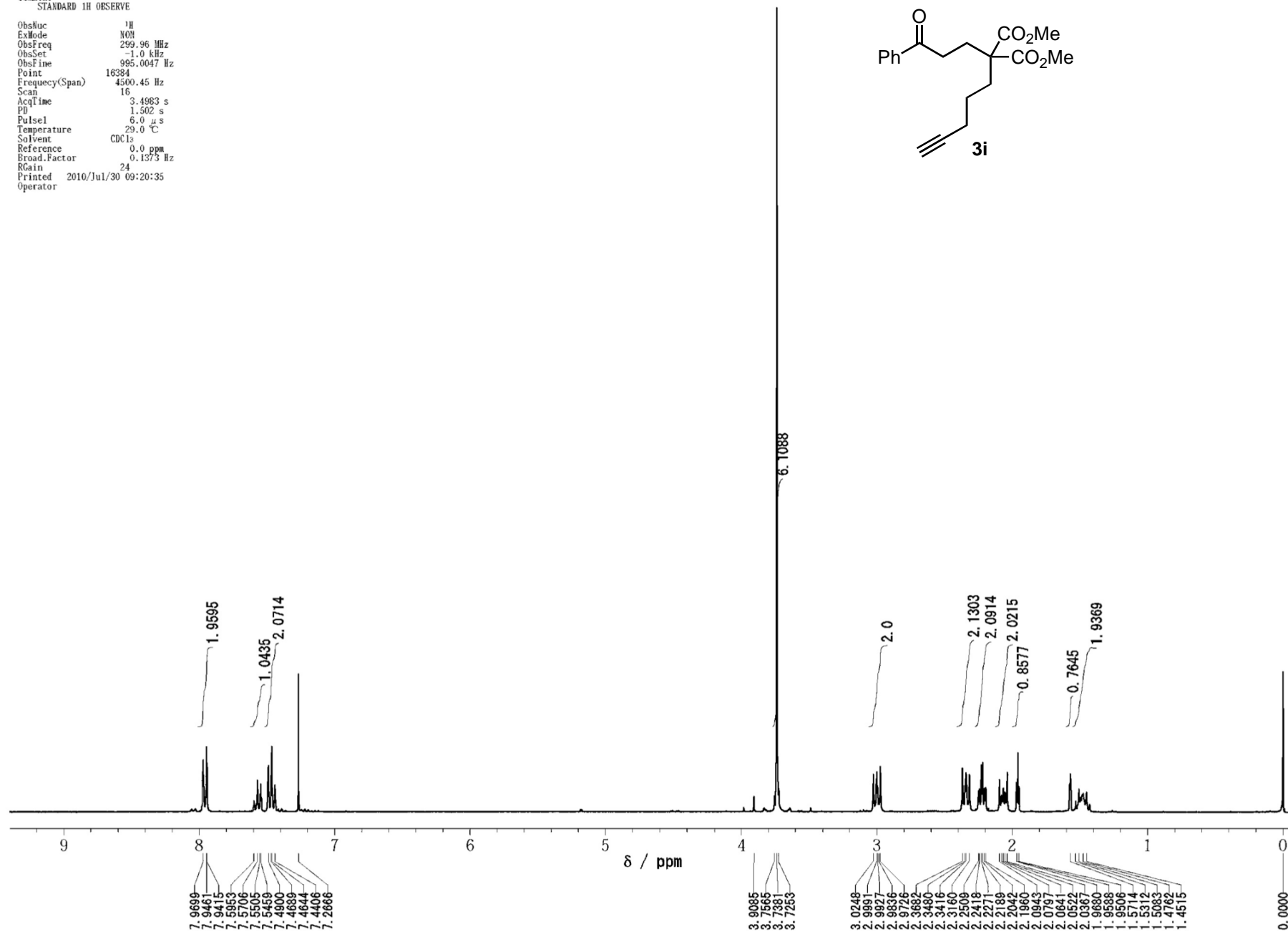
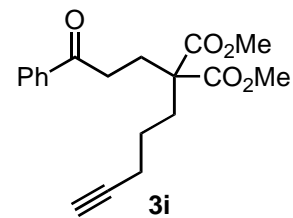


Original File:
 Date Jun 9 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 192
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 22:24:19
 Operator

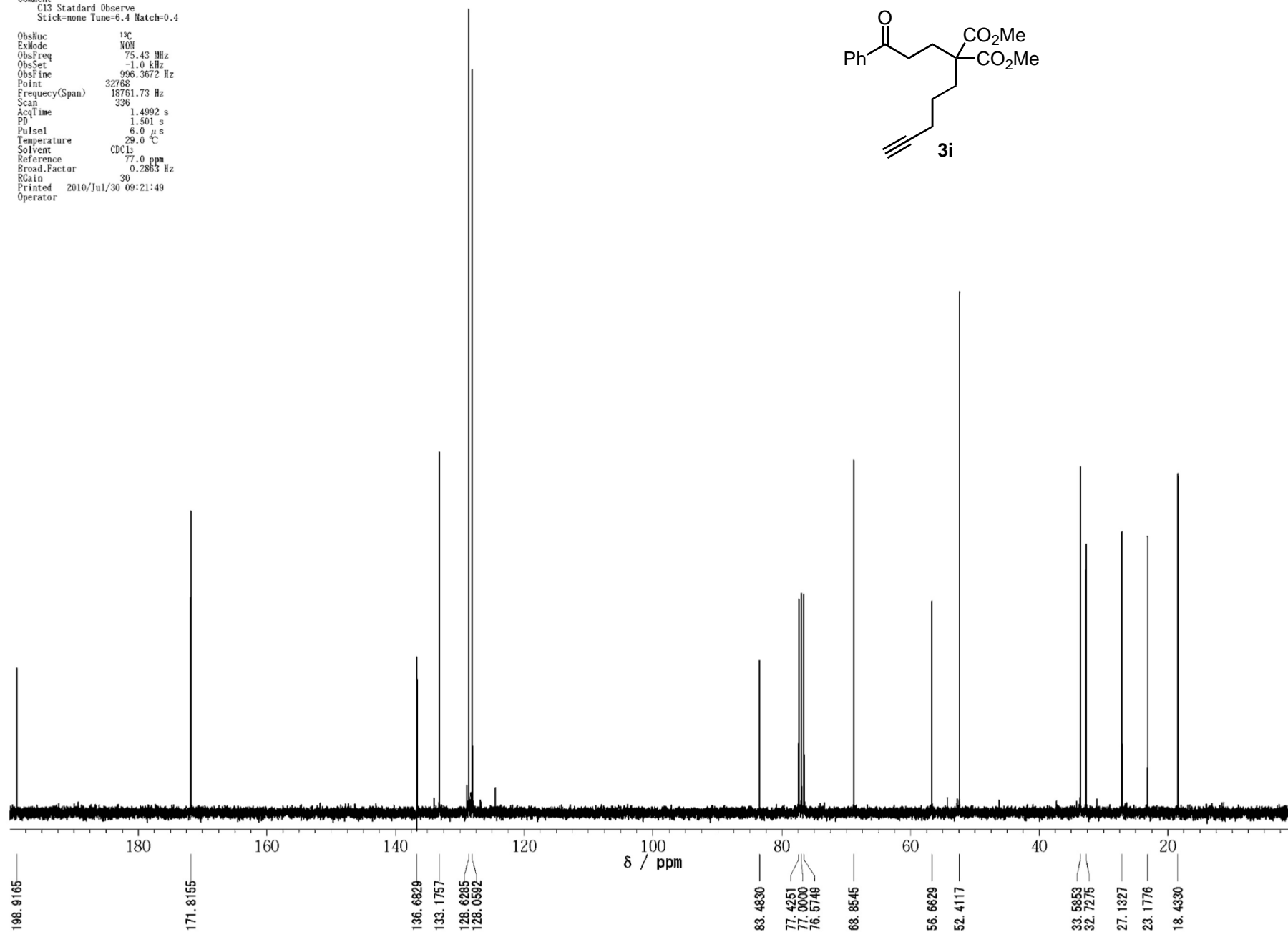
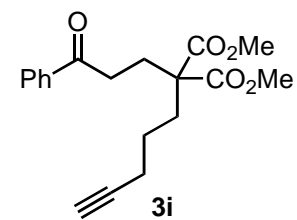


Original File:
 Date Feb 20 10
 Comment
 STANDARD 1H OBSERVE
 ObsRuoc ¹H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 16
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/30 09:20:35
 Operator

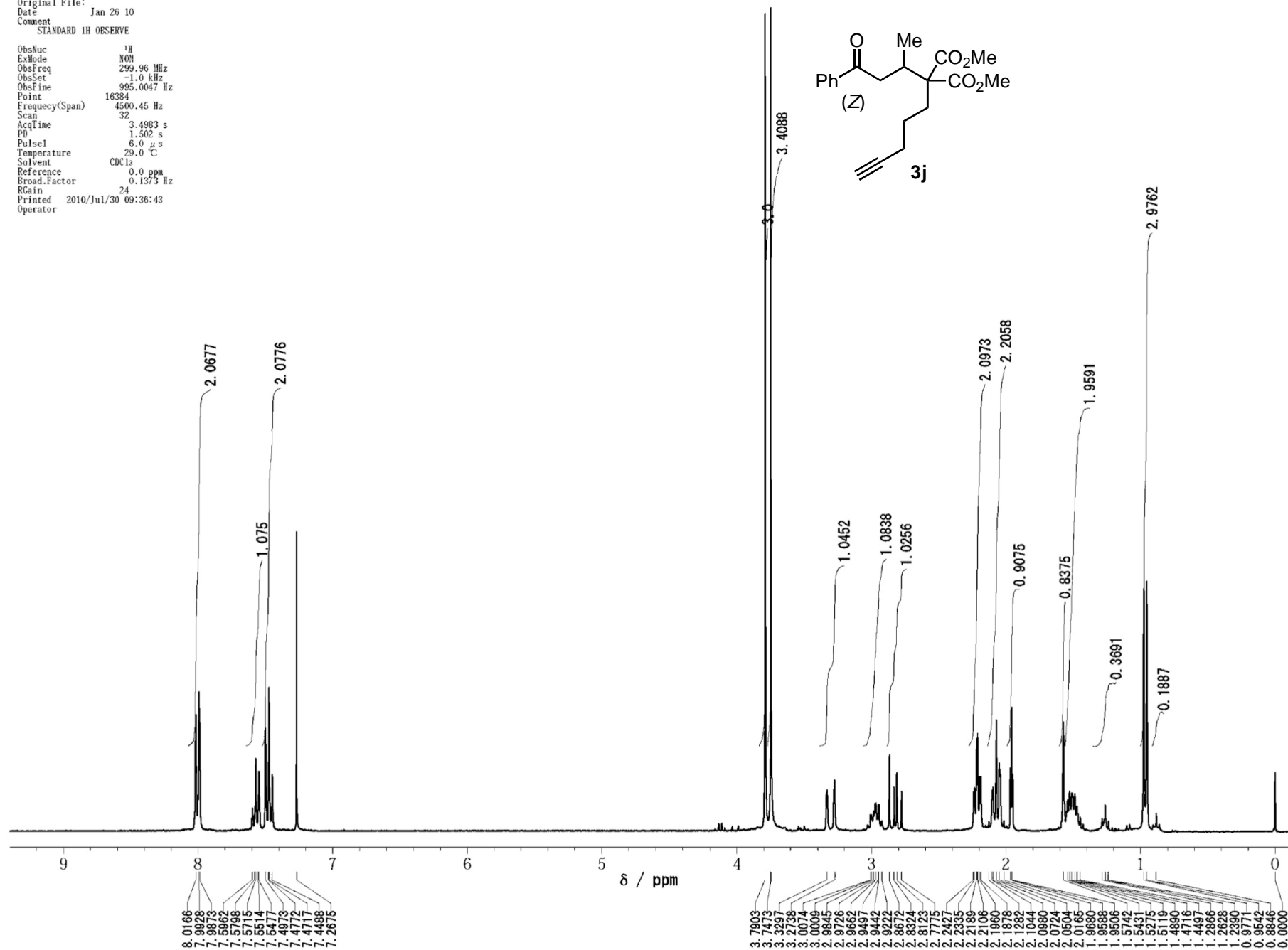
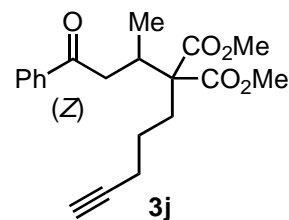


Original File:
 Date Feb 20 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 336
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 09:21:49
 Operator

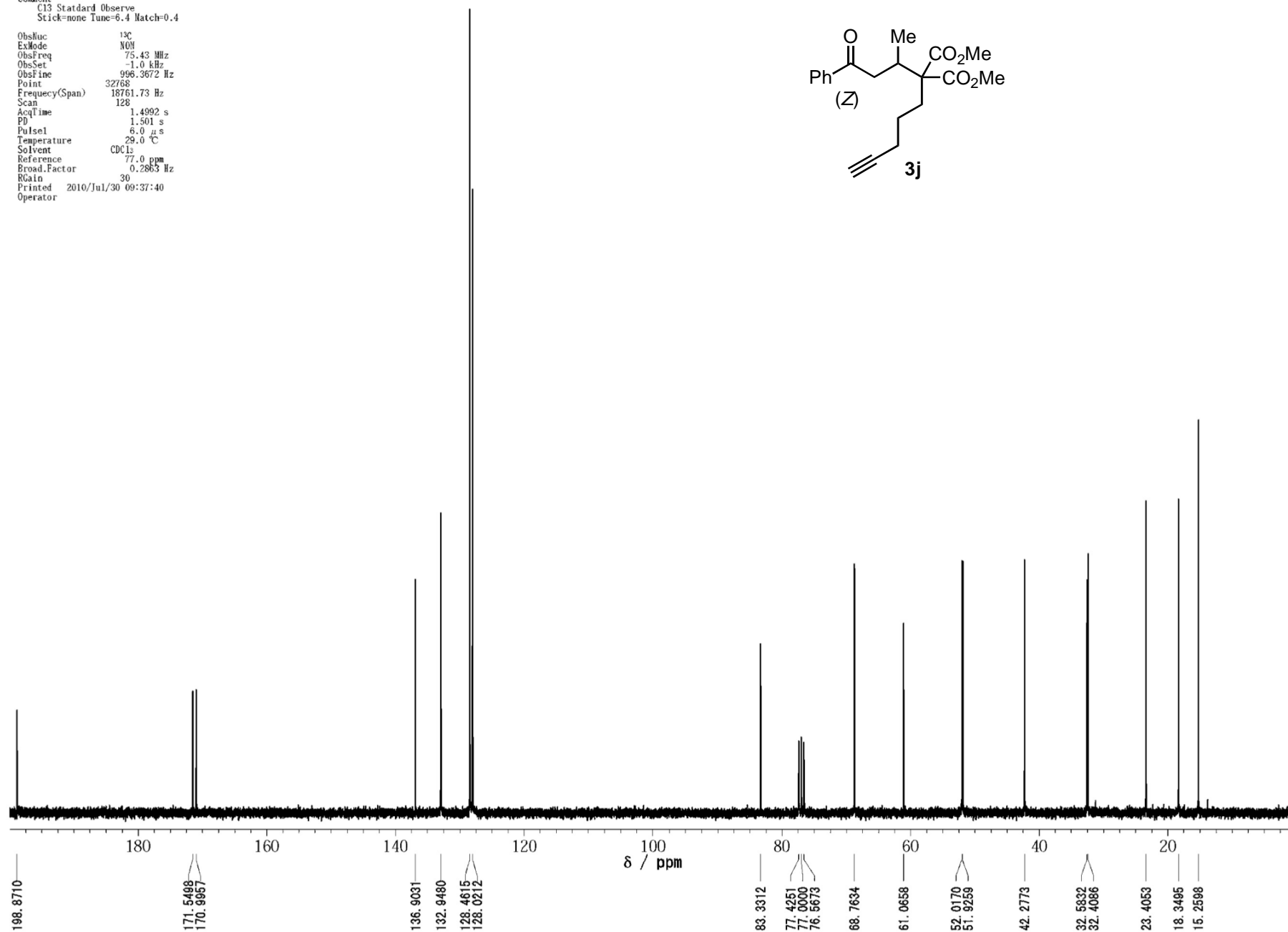
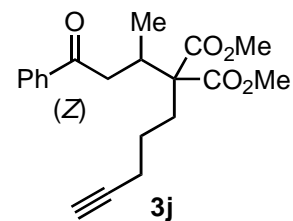


Original File: Jan 26 10
 Date
 Comment
 STANDARD 1H OBSERVE
 ObsMod 1H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/30 09:36:43
 Operator

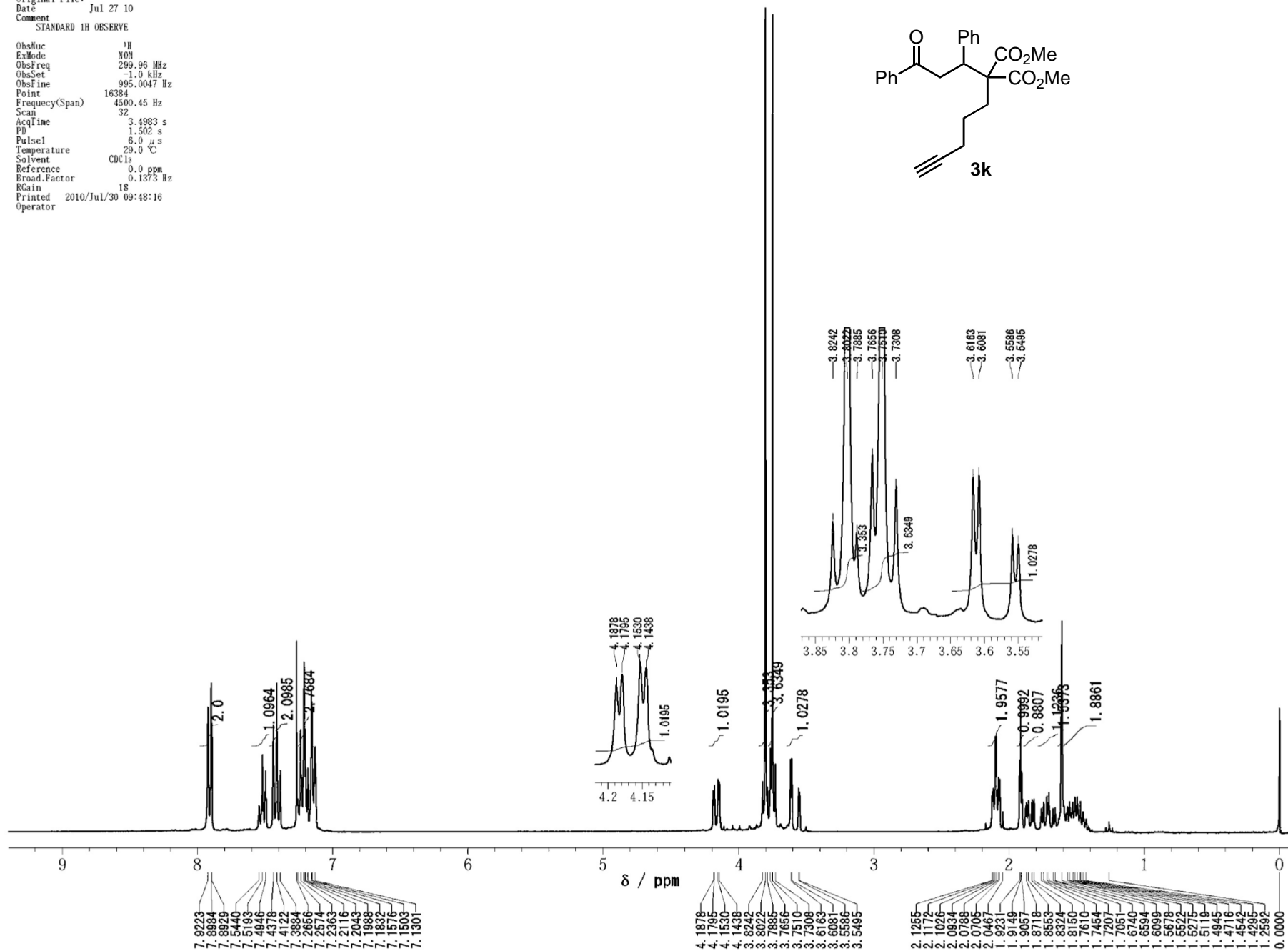
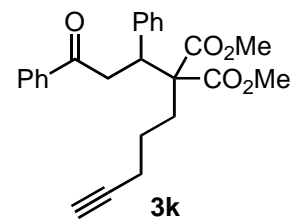


Original File:
 Date Jan 26 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 128
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 09:37:40
 Operator

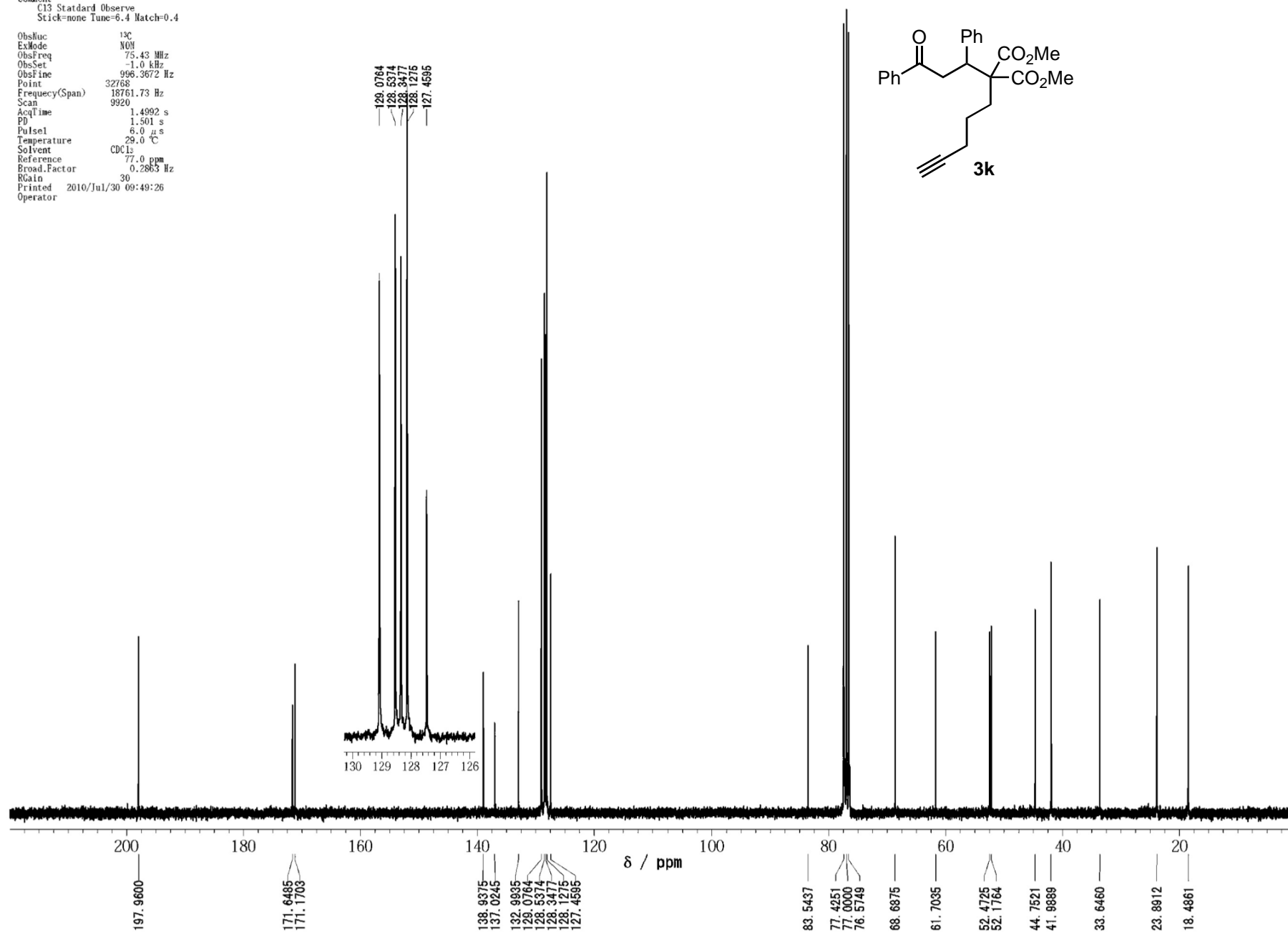
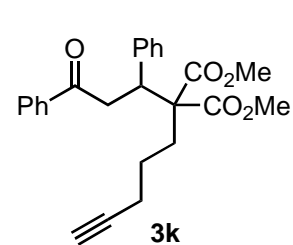


Original File: Jul 27 10
 Date
 Comment
 STANDARD 1H OBSERVE
 ObsRuoc ¹H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 0.0 ppm
 Broad.Factor 0.1373 Hz
 RGain 18
 Printed 2010/Jul/30 09:48:16
 Operator

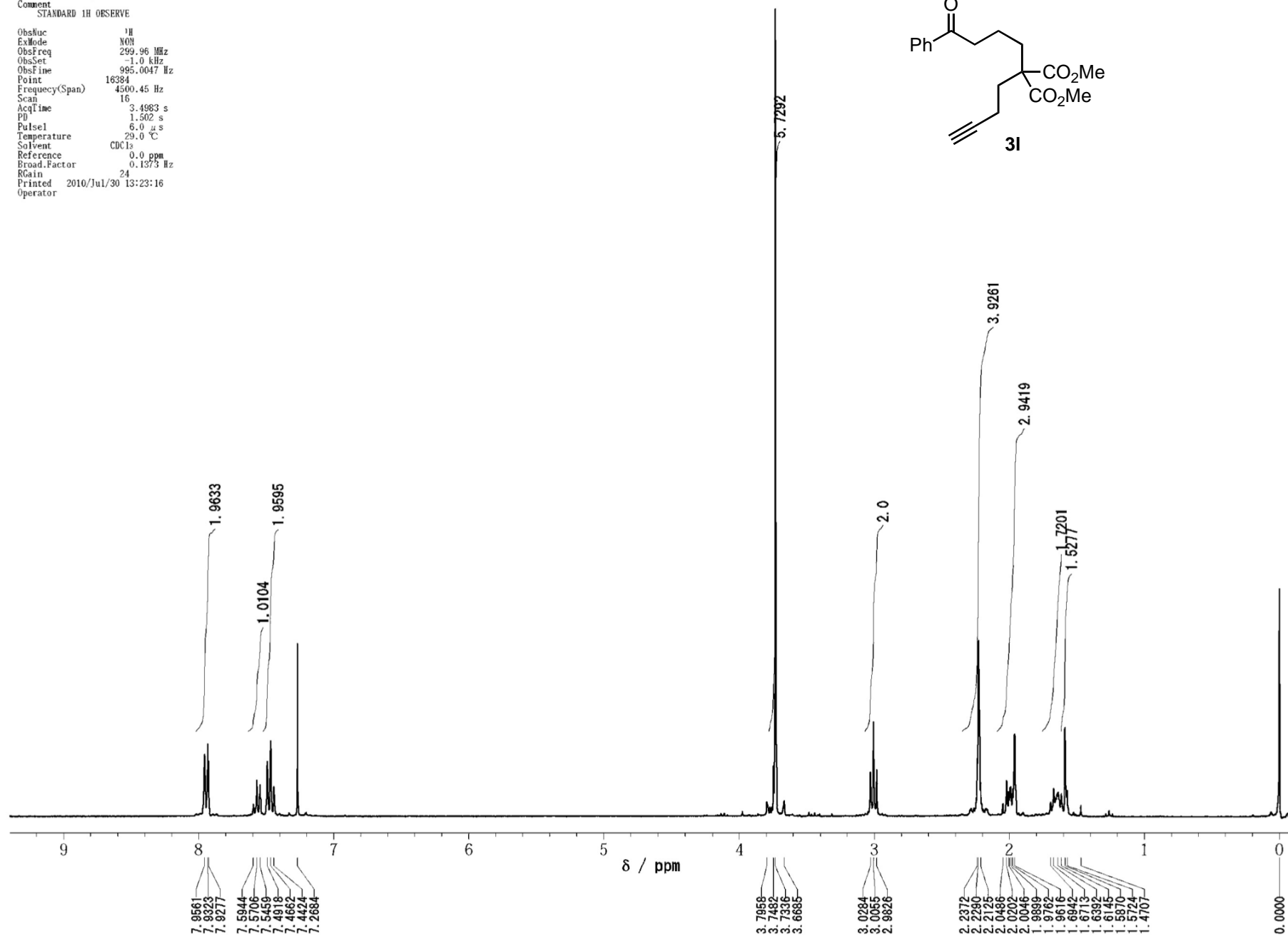
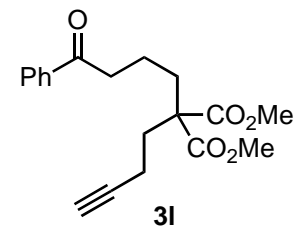


Original File:
 Date Jul 27 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 9920
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 09:49:26
 Operator

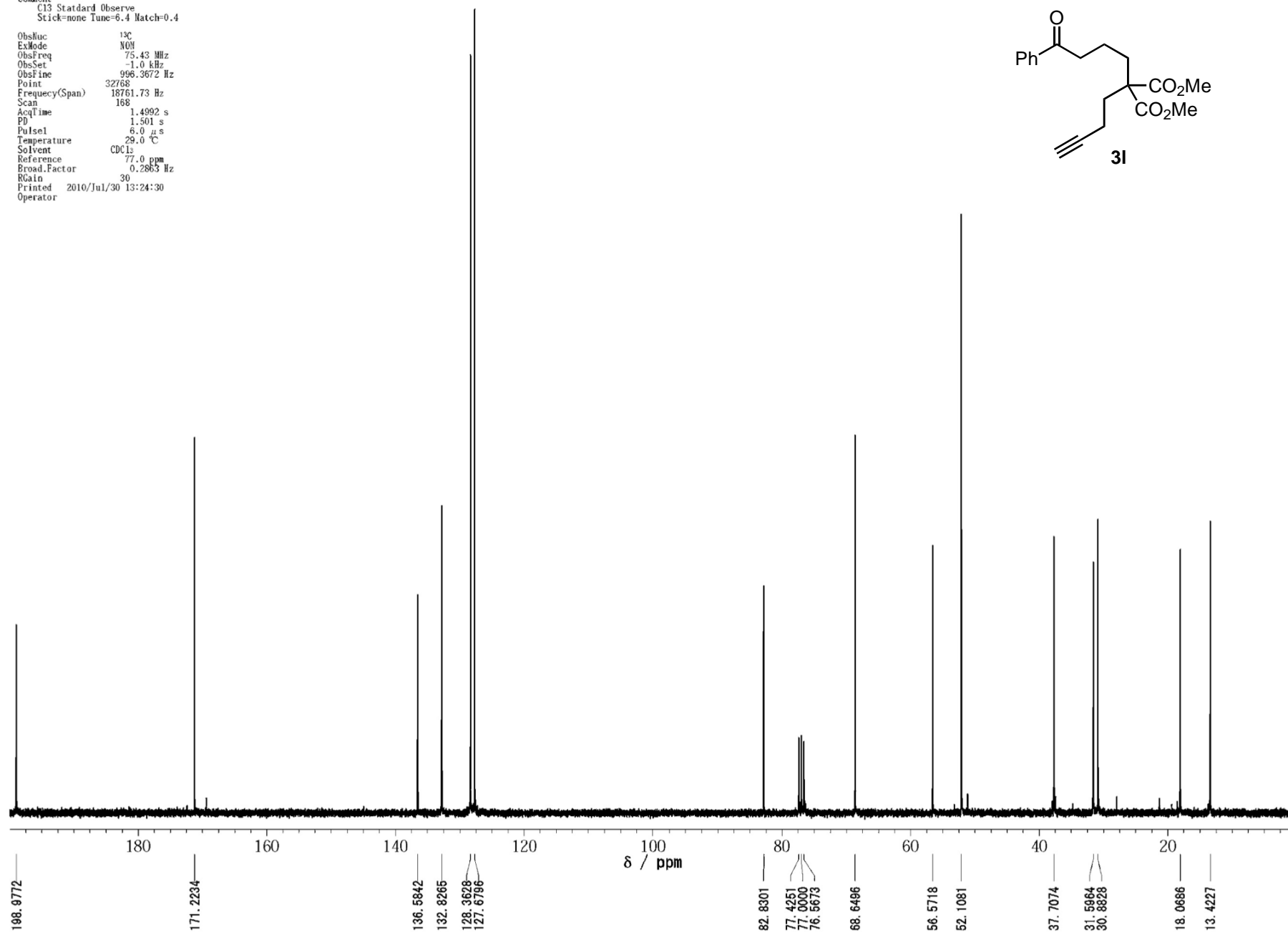
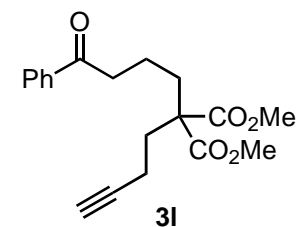


Original File: Jun 14 10
 Date: Jun 14 10
 Comment: STANDARD 1H OBSERVE
 ObsRuoc: 1H
 ExMode: NMR
 ObsFreq: 299.96 MHz
 ObsSet: -1.0 kHz
 ObsFine: 995.0047 Hz
 Point: 16384
 Frequency(Span): 4500.45 Hz
 Scan: 16
 AcqTime: 3.4983 s
 PD: 1.502 s
 Pulse1: 6.0 μ s
 Temperature: 29.0 $^{\circ}$ C
 Solvent: CDCl₃
 Reference: 0.0 ppm
 Broad.Factor: 0.1373 Hz
 RGain: 24
 Printed: 2010/Jul/30 13:23:16
 Operator:

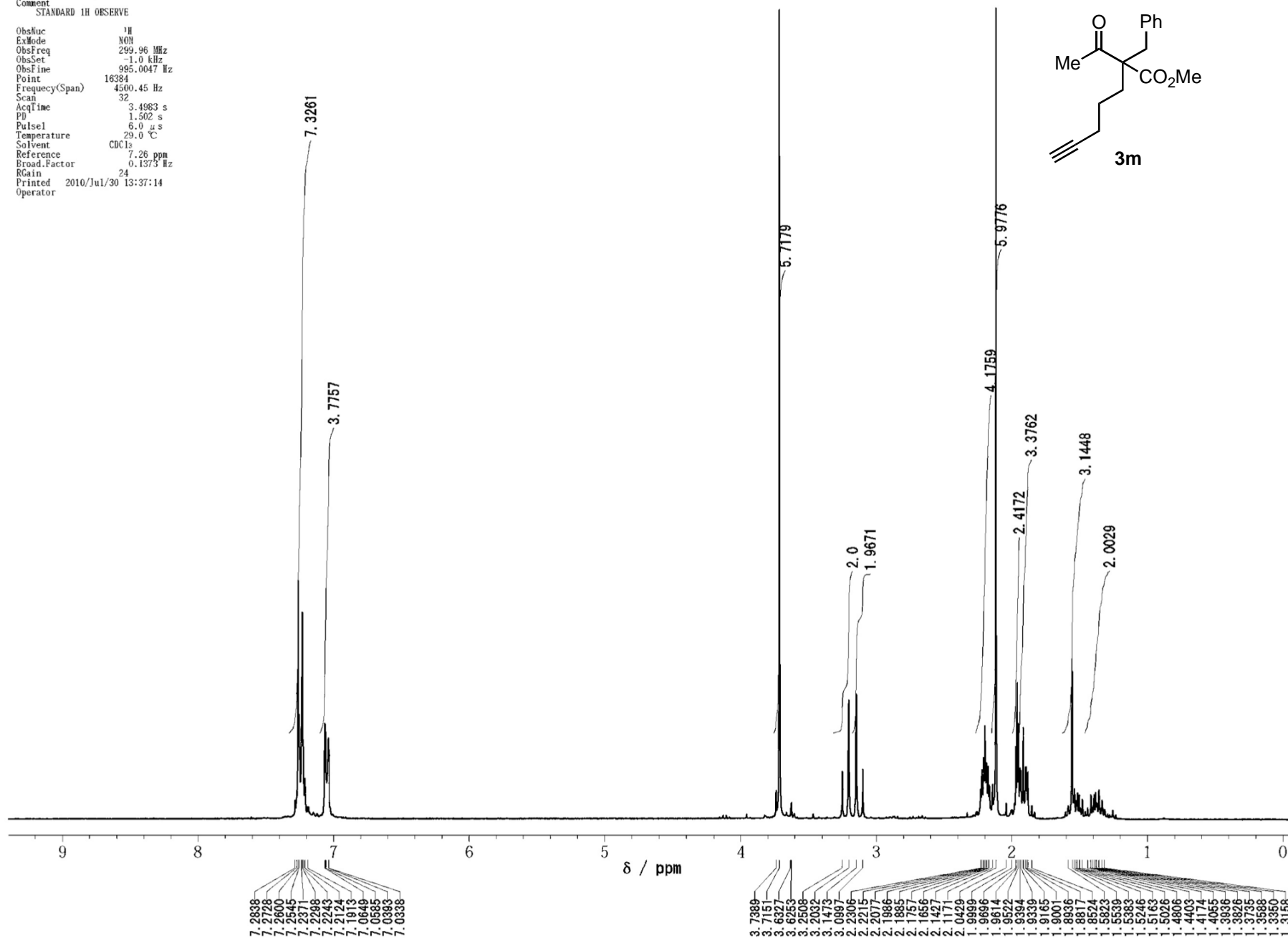


Original File:
 Date Jun 14 10
 Comment
 C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 168
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/30 13:24:30
 Operator

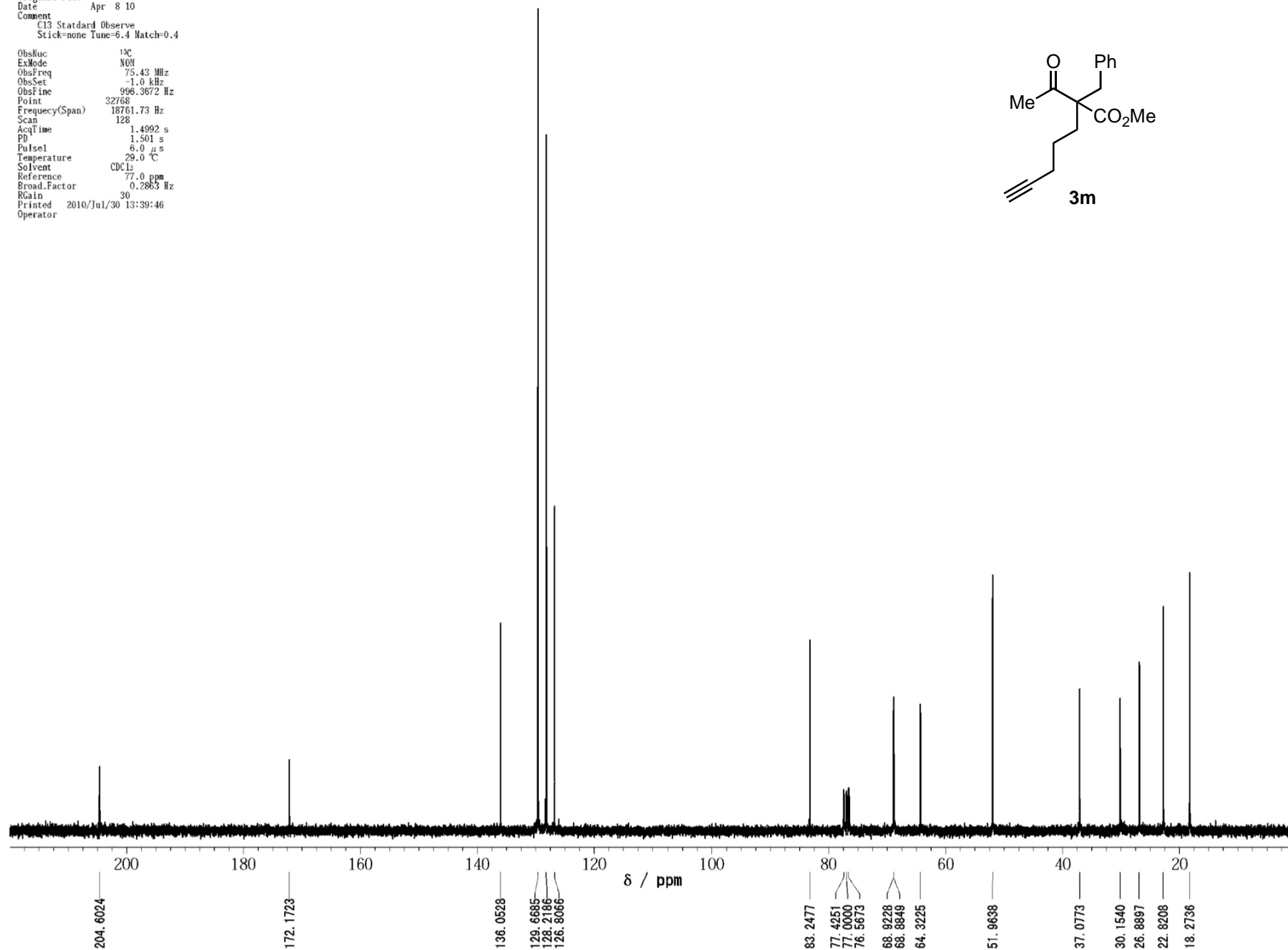
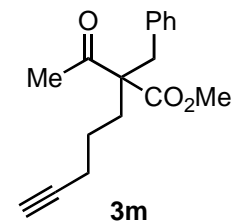


Original File:
 Date Apr 8 10
 Comment
 STANDARD 1H OBSERVE
 ObsRuoc 1H
 ExMode NMR
 ObsFreq 299.96 MHz
 ObsSet -1.0 kHz
 ObsFine 995.0047 Hz
 Point 16384
 Frequency(Span) 4500.45 Hz
 Scan 32
 AcqTime 3.4983 s
 PD 1.502 s
 Pulse1 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 7.26 ppm
 Broad.Factor 0.1373 Hz
 RGain 24
 Printed 2010/Jul/30 13:37:14
 Operator



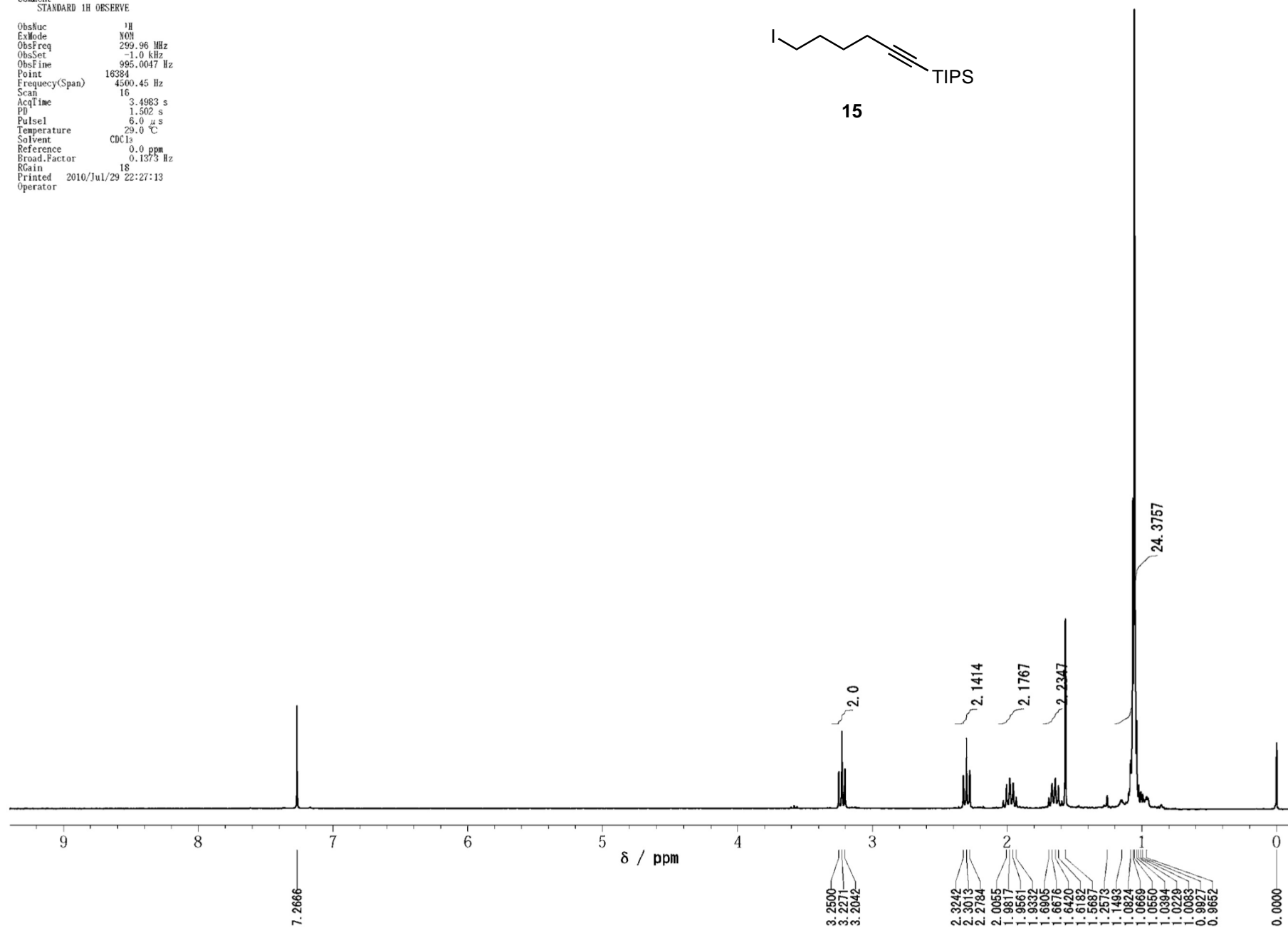
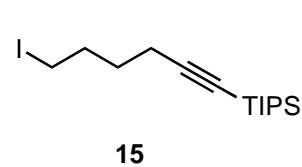
Original File:
Date Apr 8 10
Comment
C13 Standard Observe
Stick=none Tune=6.4 Match=0.4

ObsRuc 13C
ExMode NOM
ObsFreq 75.43 MHz
ObsSet -1.0 kHz
ObsFine 996.3672 Hz
Point 32768
Frequency(Span) 18761.73 Hz
Scan 128
AcqTime 1.4992 s
PD 1.501 s
Pulse1 6.0 μ s
Temperature 29.0 $^{\circ}$ C
Solvent CDCl₃
Reference 77.0 ppm
Broad.Factor 0.2863 Hz
RGain 30
Printed 2010/Jul/30 13:39:46
Operator



Original File:
Date Jun 25 10
Comment
STANDARD 1H OBSERVE

ObsMod	1H
ExMode	NOM
ObsFreq	299.96 MHz
ObsSet	-1.0 kHz
ObsFine	995.0047 Hz
Point	16384
Frequency(Span)	4500.45 Hz
Scan	15
AcqTime	3.4983 s
PD	1.502 s
Pulse1	6.0 μ s
Temperature	29.0 $^{\circ}$ C
Solvent	CDCl ₃
Reference	0.0 ppm
Broad.Factor	0.1373 Hz
RGain	18
Printed	2010/Jul/29 22:27:13
Operator	



Original File:
 Date Jun 25 10
 Comment C13 Standard Observe
 Stick=none Tune=6.4 Match=0.4

ObsRoc 13C
 ExMode NOM
 ObsFreq 75.43 MHz
 ObsSet -1.0 kHz
 ObsFine 996.3672 Hz
 Point 32768
 Frequency(Span) 18761.73 Hz
 Scan 48
 AcqTime 1.4992 s
 PD 1.501 s
 Pulse 6.0 μ s
 Temperature 29.0 $^{\circ}$ C
 Solvent CDCl₃
 Reference 77.0 ppm
 Broad.Factor 0.2863 Hz
 RGain 30
 Printed 2010/Jul/29 22:28:45
 Operator

